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A Method for the Fractionation of Oligopeptides Based on their Molecular Sizes

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Amino-acid sequence studies of proteins are of interest for the elucidation of mechanism of their biological activities. In any such study, a large number of peptides produced by partial hydrolysis of protein must first be separated from one another. Although several methods of their fractionation, such as ion exchange chromatography, ionophoresis based on their electrochemical properties, countercurrent distribution utilizing the difference of their partition coefficients between two immissible solvents and adsorption chromatography, are available, no method based on their molecular size is known.

Partridge[1] has suggested the molecular sieve effect of ion exchange resins as a tool for the fractionation of a series of various substances which have only different molecular sizes, and Thompson[2] showed that C-terminal leucine liberated from lysozyme by the action of carboxypeptidase could be separated from the remaining large protein fragment with the aid of strongly acidic ion exchange resin. Further, Deuel et al.[3] found that polygalacturonic, polymannuronic and polymetaphosphoric acid could be separated by such a method from their low molecular components. Richardson[4] has used ion exchange resin for the purification of crude dyestuffs which contained low molecular coupling substances. Kressman[5] has studied fundamental problems of the separation of various dyestuffs based on their ionic sizes.

The present authors attempted to establish a general method to fractionate various oligopeptides based on their hydrated molecular sizes by the molecular sieve of ion exchange resin.

It is a well-known fact that various amino acids are adsorbed on the hydrogen form of sulfonic acid type ion exchangers from neutral or slightly acidic solutions. In general, polystyrene type ion exchange resin has a three dimensional network structure corresponding to the extent of cross-linkage which is attributed to its divinylbenzene content. In order to be exchanged and adsorbed on the resin, the solute has to possess suitable polar group(s), and it has to be able to penetrate into the resin molecule and to react with it. Consequently large molecules, such as proteins, can not diffuse into highly cross-linked ion exchange resin and no adsorption will result, because the network is too small even though suitable dissociable groups are present in the solute molecules. On the contrary, small molecules will be adsorbed easily. On such a principle, when a solution of a peptide mixture is put on the top of the highly cross-linked ion exchange column which is assembled in series with stepwise decreasingly cross-linked resin columns, peptides will be adsorbed separately on the resins which possess the proper pore size respectively.

In the present study Dowex 50-X 16, X 12, X 8, X 4, X 2 and X 1 were used in order to study the behavior of some amino acids, synthetic peptides and the partial hydrolysates of modified silk fibroin[6] and casein towards ion exchange resins of various cross-linkages; it appears that this method was useful for the preliminary separation of peptides based on the difference of their molecular sizes.

Experimental

Materials.—Dowex 50-X 16 (20-50 mesh, lot 5754), X 12 (20-50 mesh, lot 8106), X 6 (20-50 mesh, lot 181), X 4 (50-100 mesh, lot 3458-40), X 2 (50-100 mesh, lot 3458-42) and X 1 (50-100 mesh, lot no. unknown) were used in the hydrogen form after several cycles from sodium to hydrogen forms have been performed.

The oxidative degradation product of silk fibroin, which was prepared by the reaction with hydrogen peroxide as described in earlier papers[6], contains only glycine, alanine and serine in

1) S. M. Partridge, *Nature*, **169**, 496 (1952).
2) A. R. Thompson, ibid., **169**, 495 (1952).
3) H. Deuel, J. Solms and L. Anayas-Weisz, *Helv. Chim. Acta*, **33**, 2171 (1950).
4) R. W. Richardson, *Nature*, **164**, 916 (1949); *J. Chem. Soc.*, **1951**, 910.
5) T. R. E. Kressman, *J. Phys. Chem.*, **56**, 118 (1952).
6) K. Narita, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **75**, 487 (1954); S. Akabori, K. Satake and K. Narita, *Proc. Japan Acad.*, **25**, 206 (1949).

molar ratio of about 5 : 4 : 1 as constituent amino acids.

Enzymatic digests of casein were kindly supplied by Daigo Nutritive Chemicals, and in this case a mixture of bovine pancreas enzymes was used as a hydrolytic agent. Whale insulin was also supplied by Shimizu Pharmaceutical Co. and various authentic amino acids were supplied by Ajinomoto Co. Ltd.

A part of synthetic peptides (DL-leucylglycylglycine and DL-alanylglycylglycine) was supplied by Professor H. Tani of Osaka University and other peptides were synthesized by one of the authors (K. Narita). To confirm the purity of peptides, these were checked with paper chromatography by the use of several solvents and it was found that these were homogeneous.

Procedure.—*Multicolumn of Dowex 50.* Six columns (inner diameter 0.9 cm.) containing, from top to bottom, Dowex 50-X 16, X 12, X 8, X 4, X 2 and X 1 respectively were assembled in series. To fractionate peptides or to investigate on which column a single peptide was mainly adsorbed, 10 ml. of sample solution was put on the top column (X 16 column), and, after the solution sank under the resin surface, the developer (water or diluted hydrochloric acid) was added with a flow rate of 0.2 ml. per min. at the lowest column (X 1 column) until the effluent amounted to 250 ml.

Water, 0.1 and 0.3% hydrochloric acid were used as solvent for peptide solutions. Prior to the addition of the peptide solution, all columns were equilibrated with the solvent by passing it through them overnight. The effluent was concentrated at 40°C in vacuo to 15 ml., transferred to a 25 ml. volumetric flask and filled with water to the marked level. After the disassembly of the multicolumn system, adsorbed peptides were eluted from each column with 2 N sodium hydroxide using the same flow rate as for the development. It was necessary to use 1.5 fold excess of the sodium ion over the total exchange capacity of the resin, in order to displace the peptide completely under the given conditions; the column was then washed with water. The eluate was collected in a 25 ml. or 50 ml. volumetric flask. Aliquots were used for total and α-amino nitrogen determinations. The analyses were performed by the micro Kjeldahl and the manometric van Slyke method respectively and the average peptide length (number of amino acids in the peptide) in the eluate was represented as follows.

$$\text{average peptide length} = \frac{\text{total nitrogen}}{\alpha\text{-amino nitrogen}}$$

When preparative fractionation of peptides in mixture is attempted, it is preferable to use 10% aqueous ammonia solution instead of sodium hydroxide solution as the eluting solvent, to avoid the trouble of desalting. The total exchange capacities of each resin column were listed in the tables. The amount of sample to be fractionated is preferably equivalent to 1/5 to 1/20 of the total exchange capacity of each resin column.

Batch method.—To get the knowledge about the maximum adsorption amount of some amino acids and peptides on the resins, a batch method was used. Into 30 ml. of the solution containing about 150 mg. of amino acid or peptide, the resin was added in an amount corresponding to the theoretical for the exchange of the entire solute, stirred occasionally, kept to stand over-night and an aliquot of the supernatant was pipetted. The amount of unadsorbed solute was estimated by ninhydrin method using color yield of each solute to leucine and the adsorbed quantity was calculated. In Table VIII the ratios of adsorbed amounts of amino acids or peptides to the sodium ion (exchange capacity) are shown.

Results and Discussion

As mentioned already, chemically modified silk fibroin contained only the neutral amino acids of small molecule, glycine, alanine and serine[6]. Consequently, in order to test the possibility of the success of fractionation of peptides based on their hydrated molecular sizes with the aid of a molecular sieve, it seemed suitable to use the partial hydrolysate of this protein. The peptide mixture obtained by hydrolysis of the sample (500 mg.) with 25 ml. of concentrated hydrochloric acid at 40°C for 2 hours was concentrated in vacuo at 40°C to 15 ml. The concentrate was diluted with four volumes of water and treated with free form of Amberlite IR-45 column to remove the remaining hydrochloric acid. The effluent was concentrated in vacuo to 30 ml. An aliquot of this concentrate was diluted with water to 20 ml. and another aliquot was adjusted to 0.1% hydrochloric acid concentration by adding diluted acid to 20 ml. Both samples were fractionated separately with the Dowex 50 multi-column system as described in the experimental section. As listed in Table I, these results satisfied the authors' expectation.

When the tendencies of adsorption of petidpes from water are compared in Table I with those from 0.1% hydrochloric acid solution, one can find that larger peptides are much more adsorbed from water than from acid solution on the same resin column. This fact suggests that the pore size in the resin molecule decreases in hydrochloric acid. It is a generally well-known fact that ion exchange resins shrink to some extent in the presence of electrolytes and that the degree of shrinkage depends upon the concentration of electrolyte in the surrounding medium. The shrinkage of low cross-linked resin is so particularly

TABLE I

THE FRACTIONATION OF PEPTIDES IN THE PARTIAL ACID HYDROLYSATE OF MODIFIED SILK FIBROIN BY MOLECULAR SIEVE

Developer*		H_2O			0.1 % HCl**		
Cross-linkage	Total exchange capacity of column meq.	Total N mg	α-NH_2 N mg	Average peptide length	Total N mg	α-NH_2 N mg	Average peptide length
X 16	9.4	16.2	6.92	2.4	5.77	2.28	2.6
12	8.6	1.85	0.58	3.2	4.18	1.65	2.4
8	9.5	1.50	0.28	5.4	5.00	1.73	3.4
4	6.1	1.50	0.17	8.8	6.23	1.11	5.6
2	3.8	0.69	0.03	23	1.67	0.26	6.4
1	1.8	0.40	0.01	40	0.71	0.08	8.4
Effluent	—	5.17	0.10	52	3.20	0.15	21.4
Total		27.3	8.09	—	26.8	7.11	—
Charged mixture		29.7	8.25	3.6	29.7	8.25	3.6
Recovery		92.7%	89.1%	3.4***	89.9%	86.1%	3.8***

* Flow rate, 0.2 ml./min.

** pH 1.7

*** The value was calculated from the analytical results.

TABLE II

THE EFFECT OF THE DEVELOPER TO THE ADSORBABILITY OF DL-ALANYLGLYCYLGLYCINE ON DOWEX 50

Developer*		H_2O		0.1 % HCl**		0.3 % HCl**	
Concentration of inflow		0.403 mM		0.314 mM		0.396 mM	
Cross-linkage	Total exchange Capacity of column meq.	Amount adsorbed mM	Per cent. adsorbed %	Amount adsorbed mM	Per cent. adsorbed %	Amount adsorbed mM	Per cent. adsorbed %
X 16	7.2	0.400	99.2	0.124	39.6	0.015	3.8
12	6.2	0	0	0.176	56.2	0.090	22.8
8	6.0	0	0	0	0	0.219	55.5
4	4.5	0	0	0	0	0.071	18.0
2	2.9	0	0	0	0	0	0
1	1.5	0	0	0	0	0	0
Total		0.400	99.2	0.300	95.8	0.395	99.8

* Flow rate, 0.2 ml./min.

** pH 1.7

*** pH 1.3

remarkable that it sometimes shrinks to about half of its initial volume. A natural consequence of the decreasing resin volume is that the pore size of network structure of the resin is decreased. Therefore, when hydrochloric acid concentration is increased, it is expected that the pore size of the resin becomes much smaller. In this respect, the behavior of DL-alanylglycylglycine in water, 0.1 and 0.3% hydrochloric acid solutions towards resin was studied. As shown in Table II, it is possible to change the pore size of the resin artificially, but to increase the acid concentration above 0.3% is not practicable because the dissociation of sulfonic acid groups of the resin will be suppressed. However, when organic acids, such as formic or acetic, are used, this defect will be avoided. The extent of the change of the pore size was remarkable in proportion to the decrease of divinylbenzene content as shown in Table I. As an alternate explanation of the above mentioned facts, one can not exclude the change of the shape and the size of the peptide in the presence of the electrolyte. However it appears probable that the change in the pore size of the resin is more important than that of the shape and the size of peptide in this case. On the other hand one must consider that the suppression of the dissociation of sulfonic acid groups in the resin molecule may cause the decrease in adsorption quantity of peptide in the acidic solution.

TABLE III

EXCHANGE CAPACITIES* OF DOWEX 50-X 16, X 12 AND X 8** IN WATER AND DILUTED HYDROCHLORIC ACID

Dowex 50	H_2O		0.1% HCl***		0.3% HCl****	
	meq.	%	meq.	%	meq.	%
X 16	3.95	(100.0)	3.82	(96.7)	3.82	(96.7)
12	3.15	(100.0)	3.07	(97.5)	3.03	(96.2)
8	3.65	(100.0)	3.51	(96.2)	3.45	(94.5)

* These were measured by batch method and the values were expressed for Na ion.
** The resins used were dried at 80°C in the hydrogen form for 10 hours.
*** pH 1.7
**** pH 1.3

But this possibility was excluded because of the finding of no marked differences between exchange capacities of the resins for the sodium ion in water and diluted hydrochloric acid as shown in Table III.

Table IV and V show various kinds of behavior of some amino acids in 0.3% hydrochloric acid towards the resin columns. Although the molecular size of L-leucine should be greater than that of L-alanine, the former was much more adsorbed on X 16 resin than the latter contrary to the authors' expectation as illustrated in Table IV. Similar phenomena were also found by the batch method

TABLE IV

ADSORPTION OF SOME AMINO ACIDS ON DOWEX 50 MULTICOLUMN SYSTEM FROM 0.3% HYDROCHLORIC ACID* SOLUTION

Amino acid		Glycine		L-Alanine		L-Leucine		L-Aspartic acid		L-Lysine	
Concentration of inflow		0.563 mM		0.503 mM		0.416 mM		0.396 mM		0.482 mM	
Cross-linkage	Total exchange capacity	A**	B***	A**	B***	A**	B***	A**	B***	A**	B***
	meq.	mM	%	mM	%	mM	%	mM	%	mM	%
X 16	7.2	0.468	6.5	0.124	1.7	0.335	4.7	0.015	0.21	0.387	5.4
12	6.2	0.093	1.5	0.388	6.3	0.065	1.0	0.018	0.29	0.020	0.34
8	6.0	0	0	0	0	0	0	0.288	4.8	0	0
4	4.5	0	0	0	0	0	0	0.041	0.91	0	0
2	2.9	0	0	0	0	0	0	0	0	0	0
1	1.5	0	0	0	0	0	0	0	0	0	0
Total		0.561		0.512		0.400		0.362		0.407	
Recovery		99.6%		101.7%		96.2%		91.4%		84.6%	

* Flow rate, 0.2 ml./min.; pH 1.3.
** Amount adsorbed.
*** Ratio of adsorption of amino acid to the Na ion.

TABLE V

ADSORPTION OF SOME PEPTIDES ON DOWEX 50 MULTICOLUMN SYSTEM FROM 0.3% HYDROCHLORIC ACID* SOLUTION

Peptide		Gly-L-Leu		DL-Leu-Gly		Gly-L-Leu-Gly		Gly-L-Leu-L-Leu		DL-Leu-Gly-Gly		DL-Ala-Gly-Gly	
Concentration of inflow		0.365 mM		0.422 mM		0.361 mM		0.230 mM		0.292 mM		0.396 mM	
Cross-linkage	Total exchange capacity	A**	B***	A**	B***	A**	B***	A**	B***	A**	B***	A**	B***
	meq.	mM	%	mM	%	mM	%	mM	%	mM	%	mM	%
X 16	7.2	0.086	1.2	0.060	0.83	0.049	0.68	0.041	0.57	0.013	0.18	0.015	0.21
12	6.2	0.241	3.9	0.210	3.4	0.227	3.7	0.148	2.4	0.080	1.3	0.090	1.4
8	6.0	0.036	0.6	0.122	2.0	0.027	0.45	0.035	0.58	0.189	3.2	0.219	3.6
4	4.5	0	0	0	0	0	0	0	0	0.011	0.24	0.071	1.6
2	2.9	0	0	0	0	0	0	0	0	0	0	0	0
1	1.5	0	0	0	0	0	0	0	0	0	0	0	0
Total		0.363		0.392		0.303		0.224		0.293		0.395	
Recovery		99.6%		93.1%		83.9%		97.5%		100.3%		99.8%	

* Flow rate, 0.2 ml./min.; pH 1.3.
** Amount adsorbed.
*** Ratio of adsorption of peptide to Na ion.

(Table VIII). To explain this fact one must consider that the hydrated molecular size of L-alanine is much larger than that of L-leucine in acid solution. In the case of L-aspartic acid, Table IV suggests that the effect of side chain carboxyl group can not be ignored under these conditions.

When the adsorption quantities of glycyl-L-leucine and DL-leucylglycine are compared with one another, it is clear that the effect of the size of the N-terminal amino acid is greater than that of the C-terminal one, as expected. The results of the tripeptides listed in Table V also satisfy the authors' expectation; namely the larger the molecular size of the peptide, the more the decrease in the adsorption quantity of peptide on the resins.

TABLE VI

THE BEHAVIOR OF WHALE INSULIN IN 0.1% HYDROCHLORIC ACID* TOWARDS DOWEX 50 MULTICOLUMN SYSTEM

Concentration of inflow 5.48 mg N

Cross-linkage	Total exchange capacity meq.	Amount adsorbed mg N	Per cent adsorbed %
X 16	7.2	>0.011	>0.2
12	6.2	>0.025	>0.5
8	6.0	>0.020	>0.4
4	4.5	0.431	7.9
2	2.9	0.683	12.6
1	1.5	1.11	20.3
Effluent	—	2.74	50.0
Total		5.01	91.4

* pH 1.7, flow rate, 0.2 ml./min.

As shown in Table VI, whale insulin was hardly ever adsorbed from 0.1% hydrochloric acid solution on high cross-linked resins. In such an acid solution, it will be considered that insulin is dissociated to monomer molecules (molecular weight 6,000). If the insulin molecule were spherical, the hydrated particle diameter could be calculated as roughly 27Å[7] from the data of Fredericq et al.[8] Thus it seems that Dowex 50-X 16, X 12 and X 8 do not have the pore of diameter of above 27Å in 0.1% hydrochloric acid solution.

In a further experiment, the authors attempted to separate the synthetic mixture of glycine, DL-leucylglycine and DL-alanylglycine in 0.3% hydrochloric acid solution from one another by the molecular sieve. After the elution of adsorbed materials with 2 N sodium hydroxide, the desalting and then one dimensional chromatography in phenol-water system, it was found that glycine was adsorbed on X 16 resin and a part on X 12 resin, DL-leucylglycine was adsorbed mostly on X 12 resin and partly on X 8 resin, and most of the tripeptide was adsorbed on X 8 and a small amount of X 4 resin.

In Table VII, two examples of the result which was obtained by the treatment of enzymatic digests of casein with molecular sieve column are listed. Digest I represents an almost completely digested mixture with an average peptide length of 1.78, while Digest II represents a partial digest mixture of average peptide length of 4.66. These data seem to show that the peptides are poorly separated. However, when the behavior of L-aspartic acid shown in Table IV is considered, one can suppose that the behavior of acidic amino acids and their peptides is not necessarily controlled only by their molecular sizes. It is a well-known fact that casein contains a large amount of acidic amino acids and especially strongly acidic phosphoserine residues. In fact, large quantities of phosphoric acid, serine, proline, aspartic and glutamic acid, leucine and alanine were detected in the complete hydrolysate of the effluent fraction which passed through the whole column system. This fact seems to indicate that the phosphopeptides in casein digests contain these amino acids, and that they are resistant to enzymatic attack as the average peptide length in the effluent fraction is quite great.

Moreover, the maximum adsorption quantities of some amino acids and peptides on resins were measured by the batch method (Table VIII). Comparing these figures with those of Table IV and V, one can see that the adsorption quantities of the solutes in column method are only 7 to 15% of those in the batch method. These facts indicate that the adsorption equilibrium is not reached at the flow rate of 0.2 ml. per min. in the column method and that for the solute to react completely with the resin a much slower rate is required. Table VIII shows that there is only a slight difference between maximum adsorption quantities of DL-leucylglycine and DL-alanylglycylglycine in 0.3% hydrochloric acid solution, but in the column method both peptides

7) The calculation was done by Dr. Y. Kawade of the Virus Research Institute, Kyoto University and the authors express their thanks to him.

8) E. Fredericq and H. Neurath, *J. Am. Chem. Soc.*, **72**, 2684 (1950).

TABLE VII
THE FRACTIONATION OF PEPTIDES IN ENZYMATIC DIGEST OF CASEIN*

Sample	Cross-linkage	Total exchange capacity	Digest I Total N	Digest I α-N_2H N	Digest I Average peptide length	Digest II Total N	Digest II α-N_2H N	Digest II Average peptide length
			mg	mg		mg	mg	
			22.98	12.90	1.78	80.24	17.24	4.66
		meq.	mg	mg		mg	mg	
	X 16	7.2	7.19	5.20	1.38**	12.34	4.73	2.51**
	12	6.2	4.94	4.26	1.16	5.71	1.78	3.21
	8	6.0	2.89	2.76	1.05	10.41	2.89	3.60
	4	4.5	1.10	0.95	1.16	25.98	6.34	4.10
	2	2.9	0.31	0.31	1.00	4.44	0.97	4.57
	1	1.5	0.0	0.0	—	1.50	0.32	4.69
Effluent		—	4.20	0.30	14.0	6.95	0.22	31.58
Total			20.63	13.78		67.33	17.25	
Recovery			89.8%	106.8%	1.49***	83.9%	100.0%	4.90***

* Developed with 0.3% hydrochloric acid, pH 1.3, at flow rate of 0.2 ml./min.
** In this fraction, basic amino acids are also contained.
*** The value was calculated from the analytical results.

TABLE VIII
MAXIMUM ADSORPTION QUANTITIES OF SOME AMINO ACIDS AND PEPTIDES ON DOWEX 50
(Figures show adsorbed solutes in percentages of exchange capacities in water.)

	Cross-linkage	H_2O	0.1% HCl*	0.3% HCl**
		%	%	%
Glycine	X 16	85.2	85.5	55.3
	12	86.9	87.7	58.0
	8	87.2	86.6	54.5
L-Alanine	X 16	—	—	32.8
	12	—	—	40.0
	8	—	—	36.1
L-Leucine	X 16	—	—	38.8
	12	—	—	48.5
	8	—	—	41.8
L-Aspartic acid	X 16	39.8	—	13.4
	12	—	—	21.4
	8	—	—	24.4
L-Lysine	X 16	—	—	37.6
	12	—	—	39.9
	8	—	—	37.1
DL-Leu-Gly	X 16	58.5	34.1	14.0
	12	78.8	46.8	22.8
	8	88.5	53.7	29.8
DL-Ala-Gly-Gly	X 16	62.4	20.2	13.8
	12	78.2	28.3	20.2
	8	85.5	35.6	24.8

* pH 1.7
** pH 1.3

are successfully separated from each other (also see Table V). This fact indicates the adsorption velocity of DL-alanylglycylglycine is lower than that of DL-leucylglycine. Contrary to the authors' expectation, this concept, unfortunately, was incompatible with experimental results

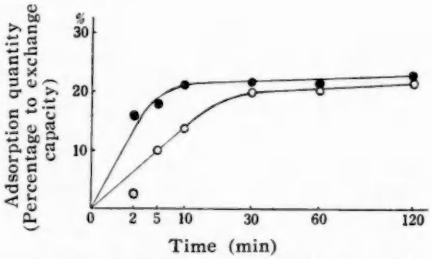

Fig. 1. The rates of adsorption of DL-alanylglycylglycine and DL-leucylglycine on Dowex 50-X 12 from 0.3 per cent. hydrochloric acid solutions.
●—● DL-Alanylglycylglycine
○—○ DL-Leucylglycine

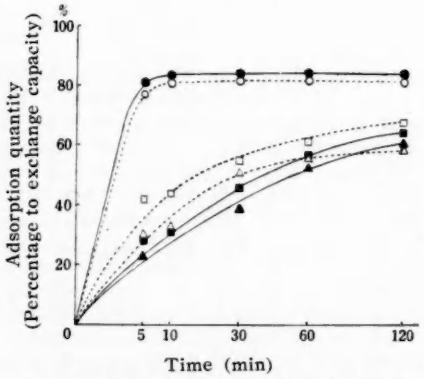

Fig. 2. The rates of adsorption of glycine, L-phenylalanine and DL-alanylglycylglycine on Dowex 50-X 16 from water. The black and the white marks show results obtained at room temperature and at 50°C respectively.
—●···○ Glycine
—■···□ L-Phenylalanine
—▲···△ DL-Alanylglycylglycine

shown in Fig. 1.

The adsorption velocities of glycine, L-phenylalanine and DL-alanylglycylglycine in aqueous solutions were also studied at room temperature (25°C) and 50°C (Fig. 2). No appreciable difference was found between velocities of low molecular glycine at either of the temperatures, while a slight difference was observed between those of L-phenylalanine and DL-alanylglycylglycine. Besides the ion exchange reaction, L-phenylalanine is adsorbed on the resin by van der Waals' force which is reduced at a high temperature, and thus aromatic amino acids may diffuse into a resin molecule easily at a higher temperature and their adsorption velocities will be increased. Generally speaking, the diffusion of solutes into the resin particles is favored by an elevated temperature. Consequently, so far as the solutes are not decomposed at high temperatures in contact with the resin, the fractionation of peptides in the column system will be much more favorable at a high temperature than at room temperature.

In the fractionation of peptides by molecular sieve, it is most important to use resins the size of whose particle is large as possible in order to reduce the surface area of the resin particle[1]; otherwise large peptides will be also adsorbed on the surface of high cross-linked resin as well as small molecular peptides. Another necessary condition is a problem of flow rate. When the flow rate is too great, the solute can not diffuse into properly cross-linked resin particles and then fractionation will be unsuccessful. By this method, not only sulfonic acid-type resins but also those of othe types may be used for peptides and another substances.

Summary

A method to fractionate peptides based on their hydrated molecular sizes by the molecular sieve effect of sulfonic-acid type ion exchange resins, Dowex 50, is described. The behavior of some amino acids, peptides and partial protein hydrolysates towards molecular sieve is also studied. Various factors which control the fractionation of solutes by molecular sieve are discussed.

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Beckmann Rearrangement in Liquid Sulfur Dioxide. III. Rearrangement by Chlorine with Various Salts

By Ritsuro TADA and Niichiro TOKURA

(Received August 28, 1957)

In a previous work[1], it was shown that the Beckmann rearrangement may be carried out by bromine only or by chlorine with a small quantity of bromine at room temperature in liquid sulfur dioxide and a possible mechanism was discussed. When chlorine was used without a catalytic amount of bromine, the rearrangement could not be induced at all. This result led the authors to examine the effect of various inorganic substances, and it now has been found that the addition of small amounts of such substances to chlorine may effect the Beckmann rearrangement in liquid sulfur dioxide.

Four groups of compounds were examined.

(1) The bromine compounds (potassium bromide, *N*-bromosuccinimide and hydrogen bromide) were the most effective, yielding 75.6, 75.2 and 67.6% of the acid amide, respectively. (2) The chlorine derivatives were the least effective. (3) Red phosphorus, sulfur and iron powder gave a moderate yield of products. (4) The effect of potassium nitrate, nitrite and cyanide was similar to that of the chlorine compounds.

The rearrangement of cyclohexanone oxime in liquid sulfur dioxide was studied at 20°C. The molar ratio of chlorine to

1) N. Tokura, R. Asami and R. Tada, *J. Am. Chem. Soc.*, **79**, 3135 (1957).

the promoter was 1 to 0.1. The results are listed in Table 1.

When compounds not easily soluble in liquid sulfur dioxide, such as phosphorus, were used, the reaction mixtures were occasionally shaken during the reaction. In the case of the bromine compounds, it was probable that the bromine liberated by the exchange reaction between chlorine and the bromine compounds promoted the rearrangement as in the previous case. The chlorine compounds were also likely to initiate the rearrangement but the yields of lactam were smaller than in the case of bromine compounds.

TABLE I

EFFECT OF CHLORINE AND INORGANIC MATERIALS OR SALTS ON THE REARRANGEMENT OF CYCLOHEXANONE OXIME IN LIQUID SULFUR DIOXIDE

Chlorine with	Yield of ε-caprolactam	
	g.	%
HBr	16.9	67.6
NaBr	6.9	27.6
KBr	18.9	75.6
N-bromosuccinimide	18.8	75.2
KI	4.1	16.4
KCl	3.2	12.8
PCl_5	5.5	22.0
S_2Cl_2	7.9	31.6
$SOCl_2$	2.9	11.6
$AlCl_3$	5.0	20.0
$FeCl_3$	2.9	11.6
$SnCl_4$	1.8	7.2
Phosphorus (red)	11.2	44.8
Sulfur	8.0	32.0
Iron powder	4.5	18.0
KNO_3	2.9	11.6
KNO_2	3.8	15.2
KCN	3.1	12.4

Cyclohexanone oxime, 25 g. (0.22 mole), liq. SO_2 200 ml., mole ratio of oxime: chlorine: salt = 1 : 1 : 0.1, reaction temp. 20°C, reaction time, one hour.

Although the solubilities in liquid sulfur dioxide were very small, sulfur and iron powder gave 32.0 and 18.0% yields, respectively. These results well coincided with 31.6 and 11.6% obtained with sulfur chloride and ferric chloride, respectively, whereas it was expected that in liquid sulfur dioxide, sulfur and chlorine might combine to form sulfur chloride and iron and chlorine to form ferric chloride. The initiation of the rearrangement by chlorine and phosphorus was explicable by the formation of phosphorus chloride followed by the decomposition of the latter to phosphorus oxychloride and thionyl chloride in liquid sulfur dioxide.

The mixture of the oxime, chlorine and an added promoter salt in liquid sulfur dioxide turned blue or bluish green in color, indicating the formation of a chloronitroso compound, while, hydrogen bromide, potassium bromide, *N*-bromosuccinimide, sulfur chloride or sulfur gave a reaction mixture reddish brown to orange in color, showing the absence of the chloro-nitroso radical, and the rearrangement was more profound than in the cases using a salt. The rearrangement was not improved by the addition of potassium nitrate, nitrite or cyanide.

Experimental

Reagents.—Cyclohexanone oxime was prepared according to the description of "Organic Syntheses"[2], m.p. 89.5—90.5°C. The salts and the inorganic materials were of the commercial purest grade, and used without further purification. Commercial chlorine from a cylinder was treated with concentrated sulfuric acid and distilled. Liquid sulfur dioxide was dehydrated with concentrated sulfuric acid, but it brought about no difference upon the results whether it was dehydrated or not.

Apparatus and the general procedure.—Glass pressure bottles, 300 ml. capacity, were used. Liquid sulfur dioxide (100 ml.) was added to the oxime (25 g., 0.22 mole) with cooling and a solution (100 ml.) containing chlorine (15.8 g., 0.22 mole) with a small definite amount (0.022 mole) of a promoter (one of the inorganic substances) was added. In experiments with a sparingly soluble material such as sulfur or sodium bromide, the cyclohexanone oxime solution was added to the chlorine solution. The mixture was allowed to stand, with occasional shaking when the mixture was not homogeneous or the reagent was difficultly soluble, for one hour at 20°C. Then the mixture was added to water with cooling and the solvent was allowed to evaporate. The residue was neutralized with diluted sodium hydroxide solution and the products were extracted with chloroform. After removal of the solvent, the residue was distilled under a reduced pressure to yield cyclohexanone (b.p. 55~65°C/35~36 mm.), unchanged oxime (b.p. 95~115°C/10~11 mm.) and ε-caprolactam (b.p. 120~130°C/7~8 mm.). The ε-caprolactam was recrystallized from ether, m.p. 67~68°C. It was identified as ε-benzoylamino-caproic acid, m.p. and mixed m.p. 80~80.5°C.

Rearrangement by chlorine with various reagents.—*Hydrogen bromide.* Liquid sulfur dioxide solution of anhydrous hydrogen bromide (0.022 mole) was prepared by separating the upper layer of the reaction mixture from 1.8 g. (0.011

2) E. W. Bonsquet, "Org. Synth.", **11**, 56 (1931).

mole) of bromine, 0.4 g. (0.022 mole) of water and 100 ml. of liquid sulfur dioxide. When chlorine mixed with the solution was added to the oxime solution, the reddish-orange reaction mixture produced 16.9 g. of ε-caprolactam. Yield 67.6% of the theory.

Sodium bromide. To a mixture of 15.8 g. of chlorine and 2.3 g. of sodium bromide in liquid sulfur dioxide a solution of cyclohexanone oxime in liquid sulfur dioxide was added. The reaction mixture turned blue in color and an insoluble powder precipitated. Treatment as described above gave 6.9 g. of ε-caprolactam. Yield 27.6%.

Potassium bromide. Chlorine and 2.7 g. of potassium bromide in liquid sulfur dioxide afforded 18.9 g. of ε-caprolactam (75.6%). The sulfur dioxide solution was reddish orange in color with fine fibrous precipitates.

N-Bromosuccinimide. This reagent (4.0 g.) gave a transparent solution pale reddish-orange in color with fine white precipitates, which afforded 18.8 g. of ε-caprolactam. Yield 75.2%.

Potassium iodide. ε-Caprolactam (4.1 g., 16.4%) was obtained from the reaction mixture of green emulsion by using 3.7 g. of potassium iodide.

Potassium chloride. By the use of 1.7 g of potassium chloride the reaction mixture became blue in color and gave a small amount of a powder and yielded 3.2 g. (12.8%) of ε-caprolactam.

Phosphorus pentachloride. From the blue reaction mixture from 4.7 g. of phosphorus pentachloride, 5.5 g. of ε-caprolactam (22.0%) was obtained.

Sulfur chloride. By the use of 3.0 g. of sulfur chloride, the pale blue, turbid, reaction mixture afforded 7.9 g. of ε-caprolactam (31.6%).

Thionyl chloride. To the solution of the oxime in liquid sulfur dioxide, chlorine with 2.7 g. of thionyl chloride in liquid sulfur dioxide was added and the resulting pale blue reaction mixture gave 2.9 g. (11.6%) of ε-caprolactam.

Aluminum chloride. By the use of 3.0 g. of aluminum chloride, the blue reaction mixture afforded 5.0 g. of ε-caprolactam. Yield 20.0%.

Ferric chloride. The pale green reaction mixture from 3.7 g. of ferric chloride produced 2.9 g. of ε-caprolactam, yield 11.6%.

Stannic chloride. From a pale blue reaction mixture from 5.8 g. of stannic chloride and chlorine, 1.8 g. (7.2%) of ε-caprolactam was obtained.

Phosphorus. The pale blue reaction mixture, in which 2.8 g. of red phosphorus had been added in suspension, gave 11.2 g. (44.8%) of ε-caprolactam.

Sulfur. A dark reddish brown reaction mixture was obtained from 5.7 g. of sulfur which was difficultly soluble and afforded 8.0 g. of ε-caprolactam in 32.0% yield.

Iron. Iron powder (1.3 g.) was mixed and occasionally shaken with the reaction mixture to afford 4.5 g. (18.0%) of ε-caprolactam.

Potassium nitrate. When 2.5 g. of potassium nitrate was used, 2.9 g. (11.6%) of ε-caprolactam was obtained from the blue reaction mixture with a small white precipitate.

Potassium nitrite. ε-Caprolactam 3.8 g., 15.2% was obtained from the pale blue reaction mixture with chlorine and 2.4g. of potassium nitrite.

Potassium cyanide. By the use of 1.5 g. of potassium cyanide, the bluish green reaction mixture gave 3.1 g. of ε-caprolactam, yield 12.4%.

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Reactions of Active Methylene Compounds. II. Ester Condensation of Methyl 2-Methoxybenzoate with Phenylacetonitrile, and of each Methoxy Substitute; a New Synthetic Route to 2-Hydroxyphenyl Benzyl Ketones

By Yoshiyuki KAWASE

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In the synthesis of isoflavones, 2-hydroxyphenyl benzyl ketones (2-hydroxydeoxybenzoins) have often been used for the starting materials. The preparation of these ketones is usually carried out by the condensation of phenols with phenylacetonitriles (Hoesch reaction), or with phenylacetic acids (Nencki reaction), or with phenylacetyl chlorides (Friedel-Crafts reaction), and further by the rearrangement of phenyl phenylacetates (Fries reaction). The position of the acyl group entering in the phenol nucleus is restricted by the effects of substitutes, and in some cases another preparative method is desirable for this reason and others.

Here, a different route to make the ketones is studied, and the preparation of 2-hydroxyphenyl benzyl ketone and its methoxy substitutes (VII) is described, which involves ester condensation of methyl 2-methoxybenzoate with phenylacetonitrile and of each methoxy substitutes (I, II) followed by hydrolysis.

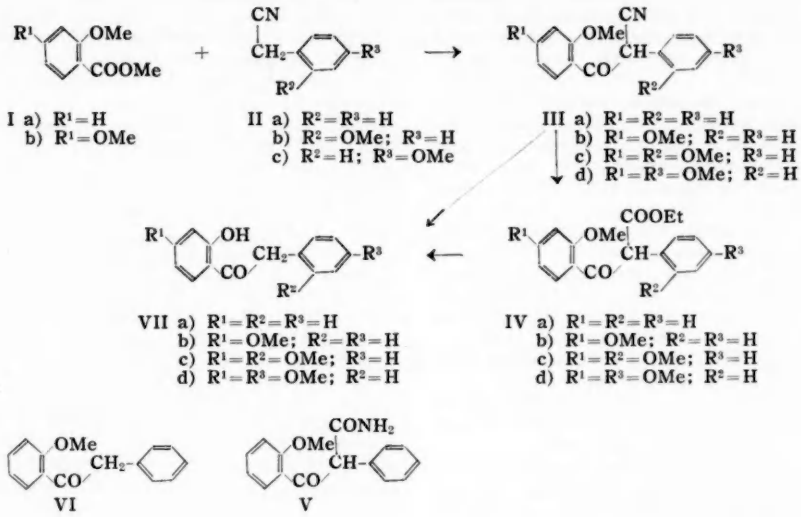
The ester condensation of unsubstituted methyl benzoate with unsubstituted phenylacetonitrile to produce benzoylphenylacetonitrile was reported long ago[1,2]. Concerning the condensation between substituted ones, however, only benzoyl-2-methoxyphenylacetonitrile was reported[3]. This reaction seems to be reversible, so it was carried out in benzene by distilling off, with the latter, the ethanol produced in the course of the reaction. 2-Methoxybenzoyl-phenylacetonitrile and its methoxy substitutes (IIIa, b, c, d) were obtained in good yield by means of sodium ethoxide or hydride. Ethyl 2-methoxybenzoyl-phenylacetate and its methoxy substitutes (IVa, b, c, d) were prepared from these nitriles by the action of hydrogen chloride in ethanol following the method similar to that reported for unsubstituted nitrile[2-4]. In the case of nitrile IIIa, 2-methoxybenzoyl-phenylacetamide (V) was obtained as by-product in poor yield. The nitriles III and the esters IV were hydrolized to the desired ketones VII by heating them with hydrochloric acid in acetic acid. In the case of hydrolysis of nitrile IIIa, the product was 2-methoxyphenyl benzyl ketone (VI), and 2-hydroxyphenyl benzyl ketone (VIIa) could be obtained under much more drastic conditions. On the other hand, hydrolysis of nitriles III by 10% aqueous sodium carbonate, and of esters IV by 10% aqueous sodium hydroxide, gave 2-methoxy- or 2,4-dimethoxybenzoic acid.

Experimental[5]

Preparation of the Nitriles III.—Sodium ethoxide prepared from 0.4~2.3 g. of sodium and 20 cc. of absolute ethanol was dried up in vacuo at 150°. To a suspension of this dried sodium ethoxide in 100 cc. of absolute benzene, a mixture of methyl methoxybenzoate and phenylacetonitrile was added and heated at 95~100° on an oil-bath for four hours, during which most of benzene was driven off together with the ethanol produced. Water was added to the well-cooled residue and the mixture was extracted with ether. The gummy product separated by acidification of the aqueous layer was washed with aqueous sodium bicarbonate and then crystallized from ethanol. In some cases, sodium hydride was employed instead of dry sodium ethoxide. The following nitriles were prepared in this way unless otherwise noted.

2-Methoxybenzoyl-phenylacetonitrile (IIIa).—Colorless needles from dilute ethanol, m.p. 108~9°;

1) R. Walther and P. G. Schickler, *J. prakt. Chem.*, (2) **55**, 308 (1897); F. Bodroux, *Bull. soc. chim.*, (4). **9**, 651 (1911); B. N. Ghosh, *J. Am. Chem. Soc.*, **109**, 117 (1916).
2) W. Wislicenus, H. Eichert and M. Marquart, *Ann.*, **436**, 92 (1925); B. W. Howk and S. M. McElvain, *J. Am. Chem. Soc.*, **54**, 286 (1932).
3) J. N. Chatterjea, *J. Indian Chem. Soc.*, **33**, 447 (1956).
4) E. P. Kohler, *J. Am. Chem. Soc.*, **46**, 1743 (1924).
5) Melting and boiling points are uncorrected.



TABLE

Product	from	reagent	reac. temp. and hr.	m.p. °C	yield %
IIIa	Ia+IIa	1 m. NaOEt	in EtOH, reflux, 4	108~9	8.
〃	〃	〃	in C_6H_6, distill., 4	〃	40.
〃	〃	2 m. NaOEt	〃	〃	70.
IIIb	Ib+IIa	1 m. NaOEt	〃	108~9	67.
〃	〃	2 m. NaH	〃	105~7	61.
IIIc	Ib+IIb	1.2 m. NaOEt	〃	114~5	42.5
〃	〃	1.7 m. NaH	〃	114~5.5	69.
IIId	Ib+IIc	1 m. NaOEt	〃	105~6	59.
IVa	IIIa	HCl—EtOH	room temp., 3 days	63~5	24.
IVa+V	〃	+1 m. H_2O	〃	67~8	56.2
IVb	IIIb	HCl—EtOH	〃	69~72	16.
〃	〃	+1 m. H_2O	〃	76~7	69.
IVc	IIIc	〃	〃	94~6	69.
IVd	IIId	〃	〃	43~50	43.5
VI	IIIa	AcOH—HCl	steam-bath, 15	oil	56.
VIIa	VI	AcOH—HBr	steam-bath, 10	56~7	61.
〃	〃	$AlCl_3$	steam-bath, 1	51~3	35.5
〃	IIIa	AcOH—HCl	steam-bath, 20	oil	47.5
〃	〃	AcOH—HBr	steam-bath, 10	53~5	34.
〃	IVa	AcOH—HCl	steam-bath, 15	oil	35.
VIIb	IIIb	〃	〃	86~7	46.5
〃	IVb	〃	〃	88~9	68.
VIIc	IIIc	〃	〃	90~1	43.
〃	IVc	〃	〃	88~9	39.5
VIId	IIId	〃	〃	100~0.5	38.
〃	IVd	〃	〃	99~100.5	33.

8.5 g. of the substance (70% yield) was obtained from 8 g. of methyl 2-methoxybenzoate (1 mole) and 5.7 g. of phenylacetonitrile (1 mole) by means of sodium ethoxide (prepared from 2.3 g. of sodium (2 moles)).

When one mole of sodium ethoxide was employed, the yield was lower (40%), and when the reaction was carried out in ethanol under reflux, the yield was poor (8%).

Anal. Found: C, 76.64; H, 5.02; N, 5.34. Calcd. for $C_{16}H_{13}O_2N$: C, 76.47; H, 5.22; N, 5.57%.

2,4-Dimethoxybenzoyl-phenylacetonitrile (IIIb).—Colorless needles, m.p. 108—9°; 8 g. of the compound (67% yield) was obtained from 8.4 g. of methyl 2,4-dimethoxybenzoate and 5 g. of phenylacetonitrile by means of sodium ethoxide (prepared from 1 g. of sodium (1 mole)).

Anal. Found: C, 72.29; H, 5.58; N, 4.74. Calcd. for $C_{17}H_{15}O_3N$: C, 72.58; H, 5.37; N, 4.98%.

By the use of 0.5 g. of sodium hydride (2 moles), the yield was 1.75 g. (61%) from 2 g. of the ester and 1.2 g. of the nitrile, m.p. 105~7°.

2, 4 - Dimethoxybenzoyl - 2 - methoxyphenylacetonitrile (IIIc).—Colorless needles, m.p. 114~5°; 1.8 g. of the compound (42.5% yield) was obtained from 2.7 g. of methyl 2,4-dimethoxybenzoate and 2 g of 2-methoxyphenylacetonitrile by acting sodium. ethoxide (prepared from 0.4 g. of sodium (1.2 mole)).

Anal. Found: C, 70.11; H, 6.10; N, 5.09. Calcd. for $C_{18}H_{17}O_4N$: C, 69.44; H, 5.50; N, 4.50%.

By the use of 0.8 g. of sodium hydride (1.7 mole), the yield was 4.2 g. (69%) from 3.8 g. of the ester and 3 g. of the nitrile, m.p. 114~5.5°.

2, 4 - Dimethoxybenzoyl - 4 - methoxyphenylacetonitrile (IIId).—Colorless needles, m.p. 105~6°; 7.8 g. of the compound (59% yield) was obtained from 8.5 g. of methyl 2,4-dimethoxybenzoate and 6.4 g. of 4-methoxyphenylacetonitrile by the use of sodium ethoxide (prepared from 1 g. of sodium (1 mole)).

Anal. Found: C, 69.54; H, 5.49; N, 4.52. Calcd. for $C_{18}H_{17}O_4N$: C, 69.44; H, 5.50; N, 4.50%.

Preparation of the Esters IV.—A solution of 1.5~3 g. of nitrile III in 50 cc. of absolute ethanol containing one mole of water was saturated with dry hydrogen chloride, and the resulting solution was allowed to stand at room temperature for three days. Water was added to the solution and ethanol was driven off in vacuo. The gummy product separated was crystallized from dilute ethanol. When the ethanolysis of the nitrile was carried out without addition of water, the yield was lower. The following esters were prepared in this way.

Ethyl 2-Methoxybenzoyl-phenylacetate (IVa).—Colorless needles, m.p. 67~8°; 1 g. of the compound (56.2% yield) was obtained from 1.5 g. of nitrile IIIa. A small amount (0.1 g.) of insoluble material was obtained, which on crystallization from a large volume of methanol gave 2-methoxybenzoyl-phenylacetamide (V), colorless microcrystals, m.p. 186~7°.

Anal. of ester IVa. Found: C, 72.69; H, 6.20. Calcd. for $C_{18}H_{18}O_4$: C, 72,46; H, 6.08%.

Anal. of amide V. Found: C, 71.64; H, 5.53; N, 5.45. Calcd. for $C_{16}H_{15}O_3N$: C, 71.36; H, 5.61; N, 5.20%.

Ethyl 2, 4 - Dimethoxybenzoyl - phenylacetate (IVb).—Colorless needles, m.p. 76~7°; 1.6 g. of the compound (69% yield) was obtained from 2 g. of nitrile IIIb.

Anal. Found: C, 69.38; H, 6.16. Calcd. for $C_{19}H_{20}O_5$: C, 69.56; H, 6.14%.

Ethyl 2,4-Dimethoxybenzoyl - 2 - methoxyphenylacetate (IVc).—Colorless needles, m.p. 94~6°; 1.6 g. of the compound (69% yield) was obtained from 2 g. of nitrile IIIc.

Anal. Found: C, 67.57; H, 6.50. Calcd. for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19%.

Ethyl 2,4-Dimethoxybenzoyl - 4 - methoxyphenylacetate (IVd).—Colorless needles, m.p. 48~50°; 1.5 g. of the compound (43.5% yield) was obtained from 3 g. of nitrile IIId.

Anal. Found: C, 66.83; H, 6.48. Calcd. for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19%.

Preparation of the Hydroxyphenyl Benzyl Ketones VII.—A solution of 0.4~2 g. of nitrile III or ester IV in 10 cc. of acetic acid containing 5 cc. of concentrated hydrochloric acid was heated on a steam-bath for fifteen hours. After being cooled, the resulting solution was made alkaline with aqueous sodium hydroxide, and the oily product separated was extracted with ether. Ether was evaporated, and the residue was recrystallized from methanol or ethanol (in some cases after distillation in high vacuum). The following ketones were prepared in this way except the case of nitrile IIIa.

2-Hydroxyphenyl Benzyl Ketone (VIIa).—a) From nitrile IIIa.—(i) Via 2-methoxyphenyl benzyl ketone (VI).—The general procedure described before gave 2-methoxyphenyl benzyl ketone (VI) in faintly yellow colored oil, b.p. 130~140°/0.001 mm., yield 0.5 g. (56%) from 1 g. of nitrile IIIa; 2,4-dinitrophenylhydrazone, m.p. 163~4°. Reported b.p. of this ketone is 198~202°/14 mm.[6].

Anal. of the hydrazone. Found: C, 61.83; H, 4.39; N, 11.25. Calcd. for $C_{21}H_{18}O_5N_4$: C, 62.06; H, 4.46; N, 13.79%.

A solution of 0.7 g. of this ketone in 8 cc. of acetic acid containing 2 cc. of 47% hydrobromic acid was heated on a steam-bath for ten hours. The resulting solution was treated as before to give ketone VIIa, colorless needles from ethanol, m.p. 56~7°, yield 0.4 g. (61%); 2,4-dinitrophenylhydrazone, m.p. 215~6° (from ethyl acetate). Reported m.p. of ketone VIIa and of its 2,4-dinitrophenylhydrazone are 60° and 219° respectively[7].

Anal. of the ketone VIIa. Found: C, 78.99; H, 5.99. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

Anal. of the hydrazone. Found: C, 61.09; H, 4.41; N, 12.23. Calcd. for $C_{20}H_{16}O_5N_4$: C, 61.22; H, 4.11; N, 14.28%.

The demethylation of ketone VI was also carried out by heating 0.6 g. of the ketone with 1 g.

6) M. Tiffeneau et al., *Bull. soc. chim.*, **49**, 1757 (1931).
7) S. Skraup and O. Binder, *Ber.*, **62**, 1127 (1929); T. C. Chadha, H. S. Mahal and K. Venkataraman, *J. Chem. Soc.*, **1933**, 1459.

of anhydrous aluminum chloride in 5 cc. of nitrobenzene on steam-bath for one hour. M.p. 51~3°, yield 0.2 g. (35.5%).

(ii) By hydrochloric acid.—A solution of 1.5 g. of nitrile IIIa in 15 cc. of acetic acid containing 10 cc. of concentrated hydrochloric acid was heated for twenty hours with addition of 5 cc. of concentrated hydrochloric acid at the intermediate time. Faintly yellow colored oil, b.p. 150~5°/0.004 mm., yield 0.6 g. (47.5%); 2,4-dinitrophenylhydrazone, m.p. 214~5°.

(iii) By hydrobromic acid.—A solution of 0.7 g. of nitrile IIIa in 8 cc. acetic acid containing 2 cc. of 47% hydrobromic acid was heated for ten hours. Colorless needles, m.p. 53~5°, yield 0.2 g. (34%).

(*b*) *From ester IVa.*—Faintly yellow colored oil, b.p. 145~150°/0.001 mm.; 0.1 g. of the compound (35% yield) was obtained from 0.4 g. of ester IVa by general method, 2,4-dinitrophenylhydrazone, m.p. 217~8°.

2-Hydroxy-4-methoxyphenyl Benzyl Ketone (VIIb).—(*a*) *From nitrile IIIb.*—Colorless needles from methanol, m.p. 86~7°, b.p. 155~165°/0.001 mm. (one distillation); 0.8 g. of the compound (46.5% yield) was obtained from 2 g. of nitrile IIIb; identical with the authentic sample (reported m.p. 90°[8]).

Anal. Found: C, 74.09; H, 5.77. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83%.

(*b*) *From ester IVb.*—Colorless needles, m.p. 88~9°; 0.5 g. of the compound (68% yield) was obtained from 1 g. of ester IVb.

2-Hydroxy-4-methoxyphenyl 2-Methoxybenzyl Ketone (VIIc).—(*a*) *From nitrile IIIc.*—Colorless needles from ethanol, m.p. 90~1°, b.p. 180°/0.001 mm. (one distillation); 0.3 g. of the compound (43% yield) was obtained from 0.8 g. of nitrile IIIc. Reported m.p. of this ketone is 93~4°[9].

Anal. Found: C, 71.15; H, 6.40. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92%.

(*b*) *From ester IVc.*—Colorless needles, m.p. 88~9°, 0.15 g. of the compound (39.5% yield) was obtained from 0.5 g. of ester IVc.

2-Hydroxy-4-methoxyphenyl 4-Methoxybenzyl Ketone (VIId).—(*a*) *From nitrile IIId.*—Recrystallization from ethanol and then from benzene yielded colorless needles, m.p. 100~100.5°, b.p. 190°/0.001 mm. (one distillation); 0.5 g. of the compound (38% yield) was obtained from 1.5 g. of nitrile IIId. Reported m.p. of this ketone is 104°[10].

Anal. Found: C, 70.84; H, 6.48. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92%.

(*b*) *From ester IVd.*—Colorless needles, m.p. 99~100.5°; 0.2 g. of the compound (33% yield) was obtained from 0.8 g. of ester IVd.

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8) W. Baker and R. Robinson, ibid., **1929**, 160.

9) P. K. Grover and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **38A**, 122 (1953); W. B. Whalley, *J. Chem. Soc.*, **1953**, 3366.

10) F. Wessely and F. Lechner, *Monatsh.*, **57**, 395 (1931).

Fractionation of Ribonuclease-resistant Fraction on ECTEOLA-cellulose

By Kentaro TANAKA

(Received November 25, 1957)

The smaller products of ribonuclease (RNase) digestion of yeast ribonucleic acid (RNA) were fractionated by Volkin and Cohn[1] using ion exchange resin and by Markham and Smith[2] using paper electrophoresis and paper chromatography. For the larger products of the digestion, however, these methods could offer little advantage for the purpose of fractionation. Recently, Bendich et al.[3] suggested the possibility of fractionating RNA-fragments which remained after treatment with RNase by ECTEOLA-cellulose columns.

In the investigation to be reported in this paper, the RNase-resistant material

1) E. Volkin and W. E. Cohn, *J. Biol. Chem.*, **205**, 767 (1953).

2) R. Markham and J. D. Smith, *Biochem. J.*, **52**, 558, 565 (1952).

3) A. Bendich, J. R. Fresco, H. S. Rosenkranz and S. M. Beiser, *J. Am. Chem. Soc.*, **77**, 3671 (1955).

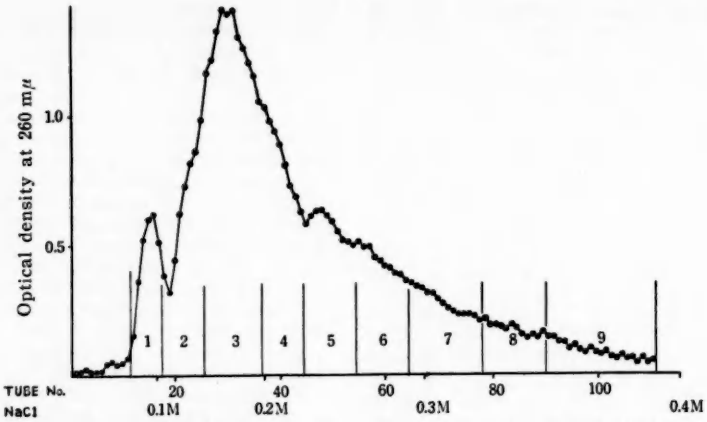

Fig. 1. Fractionation of RNase-resistant fraction of yeast RNA on ECTEOLA-cellulose by continuous gradient elution.
Exchanger: ECTEOLA-cellulose 20 g., 2.8 cm. in diameter.
Sorbed material: 200 mg. of Core 2.
Each tube contained 10 ml. of eluate. The optical density was measured after 20-fold dilution of the eluate in a 1 cm. cell. The fractions indicated with the mark | | were used for the determination of base ratio.

(Core) obtained from yeast RNA was shown to be successfully fractionated on an ECTEOLA-cellulose column. The relative molar ratio of the bases found in each fraction obtained was then measured by paper chromatography. It was thus found that oligonucelotides of larger molecular weight in the RNase-resistant material are remarkably rich in guanylic acid.

Experimental

Yeast RNA.—Commercial yeast RNA (sodium salt, Schwarz; P, 8.3%).

Pancreatic RNase.—The enzyme used in the study was a crystalline preparation obtained from Worthington Biochemical Sales Corporation.

ECTEOLA-cellulose.—The sample was prepared by Peterson and Sober's method[4] from Carl Schleicher and Schüll cellulose-powder No. 123 for column chromatography. Nitrogen content of the used sample was 0.28 meq./g. (0.39%).

Core 1.—Fifty grams of sodium salt of yeast RNA were dissolved in 500 ml. of distilled water and deproteinized by chloroform gel formation and dialyzed exhaustively. The concentrated dialyzate (250 ml.) was digested with 8.5 mg. of crystalline RNase for 18 hours at 37°C with frequent addition of sodium hydroxide solution to maintain the pH 7.2. After incubation, the reaction mixture was exhaustively dialyzed in a cellophane tubing against distilled water and then lyophilized (yield 38%). The dried material was dialyzed again in a colodium bag against distilled water and lyophilized (yield about 10%; P, 8.1%).

Core 2.—Fifty grams of sodium salt of yeast RNA were deproteinized by chloroform-gel formation, dialyzed in a cellophane tubing against distilled water, and then lyophilized (yield 52%; P, 8.2%). Fifteen grams of the dried sample were dissolved in 150 ml. of distilled water and digested with 15 mg. of crystalline RNase for 40 hours at 37°C in the presence of chloroform with frequent addition of sodium hydroxide solution to maintain the pH at 7.2. After incubation, the reaction mixture was dialyzed in a cellophane tubing against distilled water, and lyophilized (yield 11%). One gram of the dried sample was dissolved in 50 ml. of distilled water and precipitated by the addition of N hydrochloric acid to pH 1.2. The precipitate was collected by centrifuge and washed twice with 50% acetone and then with pure acetone once (yield 5.8%).

Chromatography on ECTEOLA-cellulose.—The fractionation was carried out with a column (2.8 cm. in diameter) containing 20 g. of ECTEOLA-cellulose or a column (1.2 cm. in diameter) containing 10 g. of ECTEOLA-cellulose. The column was successively washed with 1.0 N sodium hydroxide, 1.0 M dipotassium monohydrogen phosphate and 0.01 M neutral phosphate buffer before each run. The column was charged and eluted under pressure at flow rate of about 0.3 ml./cm²/min. The oligonucleotides were eluted by sodium chloride solution (in 0.01 M neutral phosphate); the concentration of sodium chloride being either continuously or stepwise increased. The continuous gradient was established in the usual way by introducing buffer containing high concentration of sodium chloride (0.5 M) into a constant volume (725 ml.) mixing chamber originally filled with the buffer. The concentration of sodium chloride in the eluate was calculated

4) E. A. Peterson and H. A. Sober, ibid., **78**, 751 (1956).

from a theoretical equation[5]. The eluates were collected in an automatic fraction collector and the amount of the oligonucleotide in each tube was determined by measuring the absorption at 260 mμ in a Beckman model DU spectrophotometer. Each peak in the elution curve was collected (as indicated in figures), dialyzed in a cellophane tubing, lyophilized and used for the determination of molar ratio of bases.

Determination of relative molar ratio of bases.—The lyophilized sample described above was hydrolyzed with 1 N hydrochloric acid at 100°C for 1 hour. The hydrolyzate was chromatographed on Tōyō 51 A filter paper with *tert*-butanol-hydrochloric acid-water as solvent. The spots were located by an ultraviolet germicidal lamp with a Kaken Ultraviolet Filter 2537*. The spots and the corresponding blanks were cut out and eluted by 0.1 N hydrochloric acid. As molar extinction coefficients for pyrimidine nucleotides and purine bases, the values published by Smith and Markham[6] were employed.

Results and Discussion

In Fig. 1 is shown the elution diagram of Core 2 when the salt concentration of the solvent was continuously increased. As can be seen from the figure, separation of the oligonucleotides in this case was not satisfactory. Nevertheless, as shown in Table I, the base ratios in fractions (indicated in Fig. 1) showed considerable changes with the progress of elution.

TABLE I

MOLAR BASE RATIOS OF THE FRACTIONS OBTAINED BY GRADIENT DEVELOPMENT CHROMATOGRAPHY ON ECTEOLA-CELLULOSE COLUMN

Sample	Base ratio*				Pu/Py
	A	G	U	C	
Core 2	10	13.7	1.7	2.6	5.5
Fraction No.**					
1	10	10.5	3.0	5.2	2.5
2	10	9.2	2.1	3.6	3.4
3	10	8.5	2.0	2.2	4.4
4	10	9.2	1.6	1.6	6.0
5	10	14.9	2.5	1.9	5.7
7	10	28.5	3.2	4.5	5.0
9	10	33.8	5.9	3.1	4.9

* A: Adenine, G: Guanine, U: Uracil, C: Cytosine

** Ref. Fig. 1

5) R. M. Bock and N. S. Ling, *Anal. Chem.*, **26**, 1543 (1954).

6) J. P. Smith and R. Markham, *Biochem. J.*, **46**, 509 (1950).

* The author is indebted to Dr. E. Iwase for his kind gift of this filter.

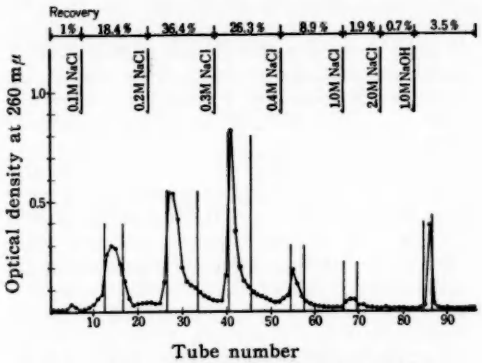

Fig. 2. Fractionation of RNase-resistant fraction of yeast RNA on ECTEOLA-cellulose by discontinuous gradient elution.
Exchanger: ECTEOLA-cellulose 20 g., 2.8 cm. in diameter.
Sorbed material: 100 mg. of Core 1.
Each tube contained ca. 13.3 ml. The volume was directly measured to calculate the recovery. The optical density was measured after 20-fold dilution of the eluate in a 1 cm. cell. The peaks indicated with the mark || were used for the determination of base ratio.

TABLE II

MOLAR BASE RATIOS OF THE FRACTIONS ELUTED FROM ECTEOLA-CELLULOSE COLUMN BY DISCONTINUOUS GRADIENT ELUTION

Sample	Base Ratio*				Pu/Py
Exp. 1**	A	G	U	C	
Core 1	10	17.8	4.2	4.4	3.2
Fraction eluted with					
0.1 M NaCl	10	11.4	5.3	6.4	1.8
0.2 M NaCl	10	9.9	2.9	2.9	3.4
0.3 M NaCl	10	28.8	3.9	4.5	4.6
0.4 M NaCl	10	32.7	4.2	3.9	5.3
1.0 M NaCl	10	28.6	—	—	—
N- NaOH	10	30.0	3.4	2.5	6.8
Exp. 2					
0.1 M NaCl	10	11.7	5.1	5.9	2.0
0.2 M NaCl	10	12.3	2.8	3.6	3.5
After rechromatography					
	10	9.8	2.5	2.4	4.0
0.3 M NaCl	10	30.2	3.5	4.2	5.2
After rechromatography					
	10	30.2	5.0	3.6	4.7
0.4 M NaCl	10	31.8	4.0	3.5	5.6
0.5 M NaCl	10	31.8	4.9	3.4	5.0

* A: Adenine, G: Guanine, U: Uracil, C: Cytosine

** Ref. Fig. 2

Further studies were carried out by means of the stepwise elution procedure. In Fig. 2 is presented one of the elution diagrams of Core 1 which was eluted by sodium chloride solutions of successively increassing concentration (in 0.01 M neutral phosphate).

As shown in Fig. 2, about 90% of the ultraviolet absorbing substance was present in the eluates of 0.1, 0.2, 0.3, 0.4 and 1.0 M sodium chloride concentration. The rest was eluted by 1.0 M sodium hydroxide.

In order to determine whether satisfactory fractionations had occurred, selected fractions were dialyzed at 4°C against distilled water, lyophilized, and rechromatographed. As shown in Fig. 3 as an example, it was found that the main peak in the elution diagram reappears in the salt concentration at which the fraction was originally eluted. The base ratios of the fractions indicated in Fig. 2 were given in Table II.

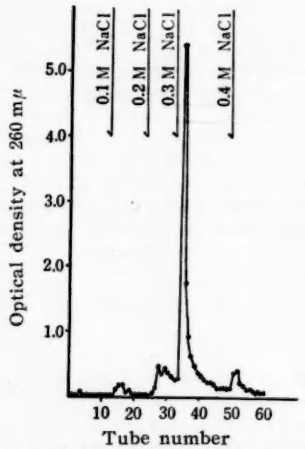

Fig. 3. Rechromatography of the fraction eluted with 0.3 M NaCl.
Exchanger: ECTEOLA-cellulose 10 g., 1.2 cm. in diameter.
Sorbed material: 0.3 M NaCl fraction of the first run. Ref. Fig. 2 (Exp. 1).
Each tube contained 10 ml. of eluate.

Pancreatic ribonuclease appears to be a highly specific phosphodiesterase which hydrolyzes secondary phosphate ester of pyrimidine ribonucleoside 3′-phosphate[7-10]. Consequently, the greater part of the oligonucleotides in RNase reistant core have only one pyrimidine nucleotide per molecule at the terminal position[1,2,8]. Thus the results presented in the Table I and II showed that as the sodium chloride concentration increases the eluate contains the larger molecular oligonucleotides as suggested by larger ratios of purine to pyrimidine. It has been shown that the whole RNase-resistant core of yeast RNA has a higher guanylic acid content than the original RNA[11,12]. The data presented here indicated that the larger molecular oligonucelotides in RNase core of yeast RNA contain increasing amounts of guanylic acid. Thus the results presented in this paper permit us to consider quite naturally that guanylic acid is not equally distributed in yeast RNA and at least some of the guanylic acid residues in the RNA are arranged in rather high molecular oligoguanylic acid structures.

Summary

RNase-resistant material obtained from yeast RNA was fractionated on an ECTEOLA-cellulose column. The elution was performed with sodium chloride-neutral phosphate buffer as solvent, the concentration of sodium chloride being increased by either gradient or stepwise procedure. Separation of oligonucleotides seemed to be affected by their molecular size. The products of larger molecular weight present in pancreatic-RNase digests of yeast RNA were very rich in guanylic acid.

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8) G. Schmidt, R. Cubiles, N. Zöllner, L. Hecht, N. Strickler, K. Seraidarian and S. J. Thannhauser, ibid. **192**, 715 (1951).
9) D. M. Brown, and A. R. Todd, *J. Chem. Soc.*, **1953**, 2010.
10) D. M. Browm, C. A. Dekker and A. R. Todd, ibid., **1952**, 2715.
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12) B. Magasanik and E. Chargaff, *Biochem. et Biophys, Acta.*, **7**, 396 (1951).

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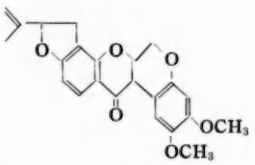
Synthesen und Konfigurationsermittlung in Rotenoid-Reihe. III. Über die Reaktion der α,β-ungesättigten Säuren mit Resorcin bzw. Phloroglucin; eine Neue Synthese des Chromanon-Rings und ein Versuch zur Synthese des Rotenons

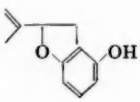
Von Masateru MIYANO und Masanao MATSUI

(Eingegangen am 20. Dezember, 1957)

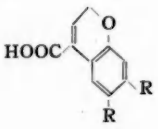
Die Kondensation von Tubanol(II) mit Toxicarsäure(III) ist, wenn es möglich wäre, wahrscheinlich das schlichteste Aufbauschema für die Synthese des Rotenons(I). Es dürfte sich bei der Kondensation um eine Synthese des Chromanon-Rings handeln.



(I)



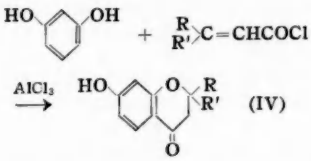
(II)



(III)

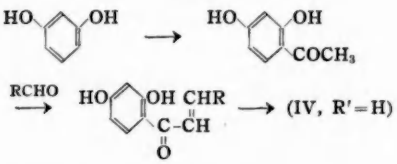
Die bisher schon bekannten Reaktionen zur Synthese von Chromanon-Ringen sind:

(1)



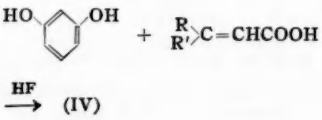
(IV)

(2)



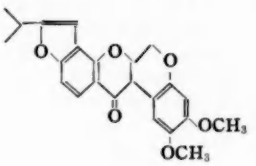
(IV, R'=H)

(3)

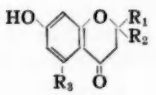


(IV)

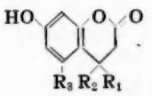
Durch die oben beschriebenen drei Methoden vielleicht gelingt es nicht die Synthese des Rotenons. Da Δ^3-Chromen-4-carbonsäure (III, R=H) in das entsprechende Säurechlorid nicht übergeführt wurde[1], muss die Darstellung des Toxicarsäure fast unmöglich sein, umso schwerer, als uns die wenigen Mengen derjenigen Säure zur Verfügung stellen. Daher ist die Reaktion(1) aussichtlos. Es ist selbstverständlich, dass die Reaktion(2) nicht verwendbar sei, insofern man die Toxicarsäure als Ausgangsmaterial braucht. Da das Rotenon gegen Säure so empfindlich ist, bei der für die Reaktion(3) notwendigen Behandlung (einstündiges Erhitzen auf 100°C in Rohr oder 7-tägiges Stehen bei Zimmertemperatur) kann die Doppelbindung von Seitenkette umlagern, um *iso*-Rotenon(V) zu liefern. Löst man das Rotenon in konzentrierte Schwefelsäure bei Zimmertemperatur geht es in *iso*-Rotenon über[2]. Kocht man das Rotenon (10 g) 5 Minuten lang mit Schwefelsäure (30 g) in Eisessig (60 g), erhält man 8.5g von reinem *iso*-Rotenon[3]. Der Vorgang beruht auf der Umlagerung der reaktionsfähigen Doppelbindung in den Hydrofuran-Ring.



(V)



(VI)



(VII)

1) H. A. Offe und W. Barkow, *Chem. Ber.*, **80**, 458(1947).
2) S. Takei, *Biochem. Z.*, **157**, 1 (1925).
3) S. Takei, M. Koide und S. Miyajima, *Ber.*, **62**, 508 (1930).

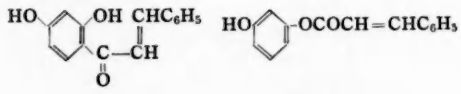
α,β-ungesättigte Carbonsäuren treten mit Phenolen unter dem Einfluss von wasserfreiem Aluminiumchlorid oder konzentrierter. Schwefelsäure nicht zu Chromanonen(VI), sondern vielmehr Dihydrocumalinen(VII) zusammen[4]. Um das Rotenon darzustellen, handelt es sich nun in erster Linie um die Möglichkeit, die auf unstabilen Verbindungen verwendbare Chromanon-Synthese aufzustellen.

Als nun wir die Kondensation der α,β-ungesättigten Carbonsäuren mit Resorcin bzw. Phloroglucin unter der Einwirkung von Antimon(III)-chlorid ausgeführt haben, in den gewissen Fällen sind die Chromanone in guter Ausbeute entstanden. Dieselbe Reaktion läuft ab, wenn auch weniger sauber, mit anderen Kondensationsmitteln wie z.B. Zinkchlorid oder Zinn(II)-chlorid.

Resorcin und die gleichen molekularen Mengen von β,β-Dimethylacrylsäure liefern beim Erhitzen auf 150°C in Gegenwart von Antimontrichlorid (oder Zinkchlorid, Zinn(II)-chlorid) 2,2-Dimethyl-7-oxy-chromanon(VI, $R_1=R_2=CH_3$, $R_3=H$)vom Schmp. 169°C(Literatur[5] zeigt 172°), das als Monoacetat vom Schmp. 91°C (identisch mit der Literatur) und 2,4-Dinitrophenylhyrazon identifiziert wird. Antimontrichlorid zeigt sich das Beste sowohl als das Kondensationsmittel auch als das Lösungsmittel (Schmp. 73°C). Arbeitet man aber mit einer ziemlich überschüssigen Menge von Dimethylacrylsäure, neben dem Chromanone entsteht ein Keton vom Schmp. 216~7°C, welches ein 2,4-Dinitrophenylhydrazon und ein Acetat vom Schmp. 113~4°C liefert. Aus dem IR-Spektrum ist es geschlossen, dass das Keton freie Oxygruppe und konjugierte Carbonyl-gruppe hat und keine unkonjugierte C=O Gruppe. Bei der Kondensation von Resorcin mit Crotonsäure, wie zu erwarten, entsteht 2-Methyl-7-oxy-chromanon (VI, $R_1=CH_3$, $R_2=R_3=H$) vom Schmp. 167~8°C, welches in das entsprechende 2,4-Dinitrophenylhydrazon übergeführt wird. In gleicher Weise umgesetzt, reagiert Phloroglucin unter der Einwirkung von Antimon(III)-chlorid mit β,β-Dimethylacrylsäure und liefert 2,2-Dimethyl-5,7-dioxy-chromanon (VI, $R_1=R_2=CH_3$, $R_3=OH$) vom Schmp. 197°C (Literatur[6] 198°C), welches in das zugehörige 2,4-Dinitrophenylhydrazon übergeführt wird.

In den oben erwähnten Fällen, ist nur die Chromanon-Ring-Verbindung isoliert worden und ausser den Ausgangsmaterialien konnten wir nichts anderer Produkte wie z.B. Dihydrocumalin (VII) aus der Mutterlauge erhalten. Bei der Reaktion von Resorcin bzw. Phloroglucin mit Zimtsäure konnten wir dagegen das Chromanon nicht erhalten. Bargellini[7] berichtete, dass beim Erhitzen von Resorcin und Zimtsäure in Gegenwart von Zinkchlorid 2',4'-Dioxy-chalkon(VIII) vom Schmp. 175°C erhalten wurde, aber Stephen[8] und Ellison[9] konnten nach dem von Bargellini angegebenen Verfahren das Chalkon nicht wieder erhalten. Wir konnten auch nichts kristallinisches Produkt isolieren bei der Kondensation mittels Zinkchlorids. Behandelt man Resorcin und Zimtsäure mit Antimon(III)-chlorid, ist farbloses Nädelchen vom Schmp. 129~130°C entstanden. Es stimmt in den Analysenzahlen mit dem Chromanon (VI, $R_1=C_6H_5$, $R_2=R_3=H$; nämlich 7-Oxyflavanon; Schmp. 240°C) oder dem Dihydrocumalin (VIII, $R_1=C_6H_5$, $R_2=R_3=H$; Schmp. 137°) über, aber aus dem IR-Spektrum ist zu entnehmen, dass es sich um den Zimtsäure-ester von Resorcin(IX) handeln dürfte. Dementsprechend wurde diese Verbindung durch alkoholische Kalilauge zur Zimtsäure verseift. Phloroglucin liefert beim Erhitzen mit Zimtsäure in Gegenwart von Antimon(III)-chlorid farbloses Nädelchen vom Schmp. 204~5°C, dessen IR-Spektrum (s. Abb. 1) nur konsequent mit dem Dihydrocumalin (VII, $R_1=C_6H_5$, $R_2=H$, $R_3=OH$) ist.

Mit der Absicht, das Rotenon darzustellen, haben wir die Kondensation von Toxicarsäure mit Tubanol unter der Einwirkung von Antimon(III)-chlorid versucht. Das Kondensationsprodukt wurde in der äthanol-löslichen (Hauptbestandteil) und äthanol-unlöslichen (Nebenprodukt, auch in Benzol unlöslich) Fraktionen abgeteilt. Aus der ersten Fraktion haben wir ein Produkt vom Schmp. 105~110°C (nicht kristallinisch) erhalten. Das IR-Spektrum



(VIII) (IX)

4) H. A. Offe und W. Barkow, *Chem. Ber.*, **80**, 474(1947).
5) W. Bridge, A. J. Crocker, T. Cubin und A. Robertson, *J. Chem. Soc.*, **1937**, 1530.
6) W. Bridge, R. G. Heyes und A. Robertson, ebenda, **1937**, 279.
7) G. Bargellini, *Atti R. Accad. Lincei*, [v], **17**, ii, 119 (1908).
8) H. Stephen, *J. Chem. Soc.*, **117**, 1530 (1920).
9) T. E. Ellison, ebenda, **1927**, 1721.

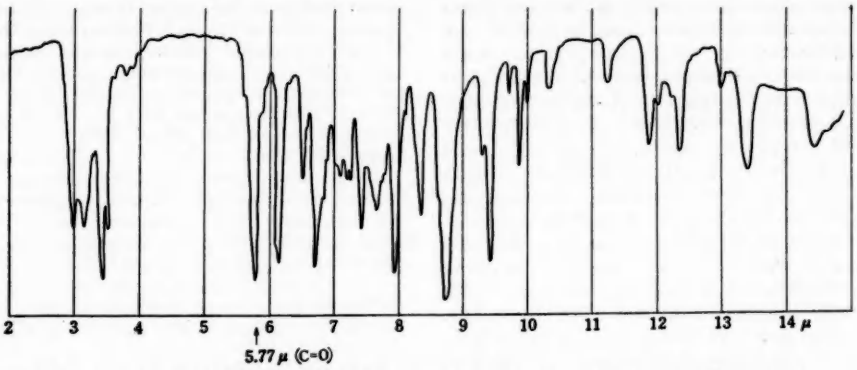


Abb. 1 4-Phenyl-5,7-dioxy-3,4-dihydro-cumalin (VII, $R_1=C_6H_5$, $R_2=H$, $R_3=OH$) in Nujol Paste.

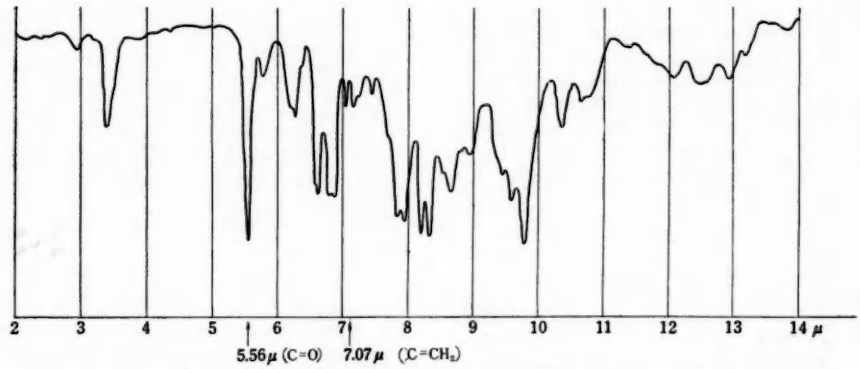


Abb. 2 Die Verbindung (X) oder (XI) oder ihre Mischung fest in KBr gepresst.

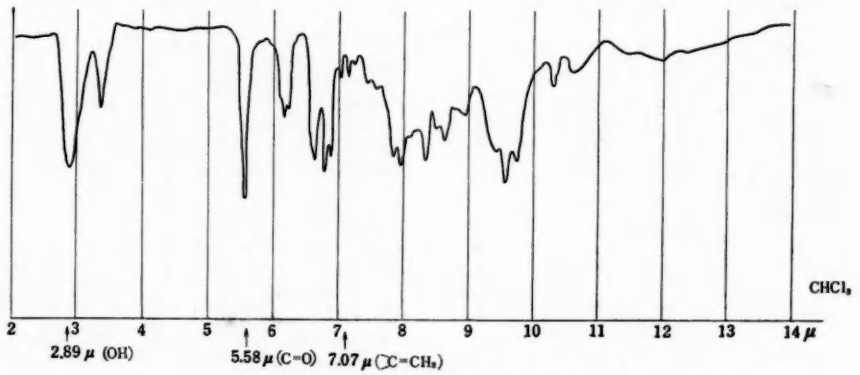
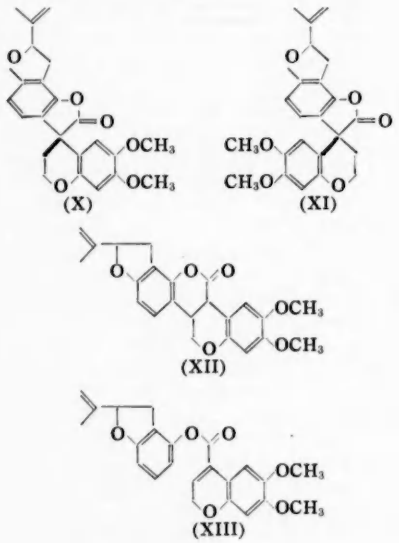


Abb. 3 Das in dem Alkohol unlösliche Nebenprodukt in Chloroformlösung.

macht die Anwesenheit eines β,γ-ungesättigten γ-Lactons (starke C=O Band in 5.56μ, s. Abb.2) sicher, dessen C=O Doppelbindung mit anderer Doppelbindung bzw. aromatischem Ringe nicht konjugieren kann. Ein mässiges Absorptionsband in 7.07μ (entspricht 7.04μ Band des Rotenons) deutet die Anwesenheit der $>C=CH_2$ Gruppe hin, obgleich die charakteristische Absorption dieser Gruppe in 11.2μ nicht vorhanden ist. Das Produkt hat keine Oxy-gruppe (sehr schwache Absorption

neben 2.9μ stammt vielleicht von wenigen Mengen Begleitstoffs). Ebenso fehlen, wie das IR-Spektrum zeigt, konjugierte Carbonyl-, Ester-, Lacton-gruppe. Ausgehend von der Überlegung von Konstitution der Ausgangsmaterialien sowie von Analysenzahlen, liegt es nahe, dass um alle bisherige Befunde befriedigend zu deuten nur die in den Formeln X und XI angegebene Struktur widerspruchlos seien. Das erhaltene Produkt besteht wohl aus beiden Verbindungen. Durch die chromatographische Reinigung konnten wir reines kristallines Material nicht erhalten. Die in der Formel XII angegebene Struktur ist nicht darum ganz unmöglich, weil es kein β,γ-ungesättigtes Lacton trägt. In der ersten Stufe vielleicht entsteht der Toxicarsäure-ester(XIII). Das aus der äthanol-unlöslichen Fraktion isolierte amorphe Produkt vom Schmp. 195～200°C bezeigt das analoge IR-Spektrum ausgenommen 2.89μ Band (OH, s. Abb. 3), daher ist es zu schliessen, dass eine oder zwei Methoxy-gruppe in dieser Verbindung durch Oxy-gruppe ersetzt werde. Gegen Bartgrundel (loach, dojô) wirken diese Produkte nicht giftig.



Beschreibung der Versuche

2,2-Dimethyl-7-oxy-chromanon (VI, $R_1=R_2=CH_3$, $R_3=H$)—*a) mittels Antimon(III)-chlorids*—Eine Mischung von 5.5 g Resorcin, 5 g β,β-Dimethylacrylsäure und 5 g Antimon(III)-chlorid wird 15 Minuten auf 140° Cerhitzt. Nach dem Erkalten nimmt man das organische Produkt mit Äther auf und wäscht die ätherische Schicht mit verd. Salzsäure (dreimal), Wasser, Bicarbonat-Lösung, schliesslich mit Wasser, dann trocknet über Natriumsulfat. Nach dem Eindampfen des Lösungsmittels erhält man 8.2 g Chromanon. Die aus heissem wässerigem Alkohol umkristallisiertten Blättchen schmelzen bei 169°C.*

Anal. Gef.: C, 68.8; H, 6.3. Ber. für $C_{11}H_{12}O_3$: C, 68.7; H, 6.3%.

Acetat—Man versetzt 1 g Chromanon in 12 ccm Pyridin mit 2 ccm Acetanhydrid und lässt 3 Tage bei Zimmertemperatur bleiben. Die Mischung wird in verd. Salzsäure gegossen, mit Äther extrahiert, mitWasser,wässeriger Kaliumcarbonatlösung, wieder mit Wasser gewaschen, nud mit Natriumsulfat getrocknet. Die beim Eindampfen des Äthers erhaltenen Kristallen werden abfiltriert, gewaschen mit Cyclohexan. Schmp. 90～91°C.

Anal. Gef.: C, 66.6; H, 6.1; Ber. für $C_{13}H_{14}O_4$: C, 66.65; H, 6.0%.

2, 4 - Dinitrophenylhydrazon — Das wird beim gewöhnlichen Verfahren erhalten und schmilzt nicht bis auf 250°C (umkristallisiert aus heissem Äthanol—Essigester(1:1). Das ist unlöslich in heissem Äthanol.

Anal. Gef.: C, 54.5; H, 4.6; N, 14.6. Ber. für $C_{17}H_{16}O_6N_4$: C, 54.8; H, 4.3; N, 15.05%.

b) mittels Zinkchlorids in Gegenwart von überschüssiger Dimethylacrylsäure—Ein Gemisch von 17 g β,β-Dimethylacrylsäure, 10 g Resorcin und 14 g Zinkchlorid wird 20 Minuten auf 150～160°C erhitzt. Nach dem Erkalten wird die Mischung mit Essigester und verd. Salzsäure geschüttelt, dann mit Ammoniumchlorid-lösung, Natriumbicarbonat-Lösung und Wasser gewaschen. Die Ester-lösung wird durch 1000 ccm 5-proz. Natronlauge extrahiert. Die gelben Blättchen, welche beim 40-stündigem Aufbewahren bei Zimmertemperatur ausgeschieden sind, werden nun abfiltriert und mit Wasser gewaschen. Das Rohprodukt (2.5 g vom Schmp. ca. 211°C) wird aus wässerigem Äthanol umkristallisiert, Schmp. 216～7°C.

Anal. Gef.: C, 72.6～8; H, 8.1～7. Ber. für $C_{27}H_{28}O_6$: C, 72.30; H, 6.29%.

Die wässerige Mutterlauge wird mit verd. Salzsäure angesauert und ausgeschiedene Kristalle werden abgesaugt, mit Wasser gewaschen. Das Rohprodukt (8.5 g vom Schmp. ca. 160°C) wird durch Umlösen aus wässerigem Alkohol gereinigt, Schmp. 168～9°C, das ist identisch mit dem in a) beschriebenen Chromanon.

2, 4 - Dinitrophenylhydrazon des Ketons vom Schmp. 216～7°C—Das wird bei der gewöhnlichen Behandlung erhalten und schmilzt nicht bis auf 250°C (umkristallisiert aus heissem Alkohol). Das ist leicht löslich in heissem Alkohol gegenüber dem 2,4-Dinitrophenylhydrazon des 2,2-Dimethyl-7-oxy-chromanon.

Anal. Gef.: C, 57.5; H, 6.5～8; N, 12.3～7. Ber. für $C_{29}H_{34}O_{12}N_8$: C, 58.2; H, 4.2; N, 13.9%.

Acetat des Ketons vom Schmp. 216～7°C — Obgleich das Keton aus alkalischer Lösung kristallisiert ist (s. oben), doch hat es freie Oxy-gruppe und liefert das Acetat. Zu einer

* Alle Schmpp. sind unkorrigiert.

Lösung des 1 g Ketons in 12 ccm Pyridin fügt man 2 ccm Acetanhydrid und 3 Tage bei Zimmertemperatur aufbewahrt. Die Mischung wird in verd. Salzsäure gegossen, mit Äther aufgenommen, mit Wasser, Kaliumcarbonat, schliesslich mit Wasser gewaschen, über Natriumsulfat getrocknet. Man vertreibt den Äther und erhält die farblosen Blättchen, welche mit wenig Cyclohexan gewaschen werden. Schmp. 113~4°C.

Anal. Gef.: C, 70.2; H, 7.1. Ber. für $C_{31}H_{32}O_8$: C, 69.9; H, 6.1%.

c) mittels Zinn(II)-chlorids—Durch Erhitzen (15 Minuten, 145°C) eines Gemisches von 5.5 g Resorcin, 5g β,β-Dimethylacrylsäure, 10g Zinn(II)-chlorid-dihydrat und die dem schon oben beschriebenen Verfahren analoge nachfolgende Behandlung erhält man 3.0 g Rohprodukt, welches nach dem Umlösen aus wässerigem Alkohol bei 169°C (0.8 g) schmilzt.

2-Methyl-7-oxy-chromanon (VI, $R_1=CH_3$, $R_2=R_3=H$)—Eine Mischung von 12 g Crotonsäure, 7 g Resorcin, 10 g Zinkchlorid wird 30 Minuten auf 170~180°C erhitzt. Nach dem Erkalten wird die erhaltene Mischung mit Äther und verd. Salzsäure stark geschüttelt, und unlösliche rote Körperchen werden abfiltriert. Die ätherische Schicht des Filtrats wird mit Ammoniumchloridlösung, Natriumbicarbonat-lösung und Wasser gewaschen, und mit Natriumsulfat getrocknet. Nach dem Umkristallisieren aus wässerigem Alkohol dann aus wässerigem Methanol erhält man farblose Blättchen vom Schmp. 167~8°C.

Anal. Gef.: C, 67.0; H, 5.9. Ber. für $C_{10}H_{10}O_3$: C, 67.4; H, 5.7%.

Das durch das gewöhnliche Verfahren erhaltene 2,4-Dinitrophenylhydrazon schmilzt nicht bis auf 250°C.

Anal. Gef.: C, 53.6; H, 4.0; N, 15.5. Ber. für $C_{16}H_{14}O_6N_4$: C, 53.6; H, 3.9; N, 15.6%.

2,2-Dimethyl-5,7-dioxy-chromanon (VI, $R_1=R_2=CH_3$, $R_3=OH$) — *a) mittels Antimon(III)-chlorids*—Eine Mischung von 1.6 g Phloroglucin (Dihydrat), 1.0 g β,β-Dimethylacrylsäure und 3 g Antimon(III)-chlorid wird 15 Minuten auf 140~145°C erhitzt. Nach dem Erkalten wird die Mischung mit Äther und verd. Salzsäure geschüttelt und die ätherische Schicht wird mit verd. Salzsäure (zweimal), Wasser, Natriumbicarbonat-lösung und wieder mit Wasser gewaschen, und mit Natriumsulfat getrocknet. Nach dem Eindampfen des Lösungsmittels und Umkristallisieren aus wässerigem Alkohol unter Aktivkohlezusatz erhält man 0.8 g Chromanon vom Schmp. 196~7°C.

Anal. Gef.: C, 63.4; H, 6.0. Ber. für $C_{11}H_{12}O_4$: C, 63.45; H, 5.8%.

2,4-Dinitrophenylhydrazon — Das wird durch gewöhnliches Verfahren erhalten und schmilzt nicht bis auf 250°.

Anal, Gef.: C, 52.8; H,4.3; N, 13.5. Ber. für $C_{17}H_{16}O_7N_4$: C, 52.6; H, 41.5; N, 14.4%

b) *mittels Zinkchlorids* — Man erhält das Chromanon (1.6 g, Schmp. 195°C) durch Erhitzen (15 Minuten, 150~160°C) und nachfolgende Behandlung aus einer Mischung von 3.2 g Phloroglucin (Dihydrat), 2.0 g Dimethylacrylsäure und 2.0 g Zinkchlorid, welches identisch mit dem durch das in a) erwähnten Verfahren erhaltenen Chromanon ist.

Kondensation von Resorcin mit Zimtsäure—Eine Mischung von 5.5 g Resorcin, 7.5 g Zimtsäure und 7.0 g Antimon (III)-chlorid wird 15 Minuten auf 140~148°C erhitzt. Nach dem Erkalten wird das erhaltene Produkt mit Äther und verd. Salzsäure stark geschüttelt und die ätherische Schicht wird mit verd. Salzsäure (zweimal), Wasser, Bicarbonat-lösung, wieder mit Wasser gewaschen, dann über Natriumsulfat getrocknet. Man vertreibt den Äther und löst das zurückbleibende Öl in wenig Benzol. Die farblosen langen Nadeln scheiden langsam aus, welche abfiltriert und aus heissem Cyclohexan umkristallisiert werden. 2.1 g, Schmp. 129~130°C.

Anal. Gef.: C, 74.0; H, 5.0. Ber. für $C_{15}H_{12}O_3$: C, 75.0; H, 5.0%.

Diese Nadeln lieferten kein 2,4-Dinitrophenylhydrazon durch gewöhnliches Verfahren. Dieses Kondensationsprodukt (0.05 g) wird in 10 ccm 10 proz. warmer alkoholischer Kalilauge gelöst und lässt sich 2 Tage bei Zimmertemperatur stehen. Nach dem Eindampfen des Alkohols sauert man es mit verd. Schwefelsäure an. Die ausgeschiedenen weissen Kristalle schmelzen bei 131~2°C (wenn gemischt mit Zimtsäure 132~3°).

Kondensation von Phloroglucin mit Zimtsäure—Eine Mischung von 1.5 g Phloroglucin (Dihydrat), 1.5 g Zimtsäure und 5.5 g Antimon (III)-chlorid wird 15 Minuten auf 140°C erhitzt. Nach dem Erkalten wird das erhaltene Produkt mit Äther und verd. Salzsäure geschüttelt und die ätherische Schicht wird mit verd. Salzsäure (zweimal), Wasser, Bicarbonat-lösung, wieder mit Wasser gewaschen, mit Natriumsulfat getrocknet. Das Lösungsmittel wird vertrieben und das zurückbleibende Öl wird mit wenig Chloroform digeriert. Die farblosen Nadeln werden aus Äther-Chloroform umkristallisiert. 0.4 g, Schmp. 204~5°C.

Anal. Gef.: C, 69.8; H, 4.7. Ber. für $C_{15}H_{12}O_4$: C, 70.3; H, 4.7%.

Die Nadeln lieferten kein 2,4-Dinitrophenylhydrazon beim gewöhnlichen Verfahren. Dieses Produkt wird durch 10 ccm 10 proz. alkoholischer Kalilauge bei Zimmertemperatur (2 Tage) verseift. Man vertreibt das Lösungsmittel und sauert mit verd. Schwefelsäure an. Das Ausgangsmaterial wird zurückerhalten.

Kondensation von Tubanol mit Toxicarsäure: Ein Versuch zur Synthese des Rotenons—Zu einer Mischung von 0.8 g Tubanol und 1.3 g Toxicarsäure in 3 ccm Dioxan fügt man 5.0 g Antimon(III)-chlorid. Man erhitzt diese Mischung 15 Minuten auf 150~160°C, während des Erhitzens dampft das Dioxan ein. Das Reaktionsprodukt wird mit Äther und verd. Salzsäure geschüttelt, mit verd. Salzsäure (zweimal), Wasser, Bicarbonat-lösung, schliesslich mit Wasser gewaschen, über Natriumsulfat getrocknet. Das Lösungsmittel wird vertrieben und das zurückbleibende Öl wird in 20 ccm heissen Äthanol gelöst und unter Aktivkohlezusatz abgesaugt. Beim 3-tägigem Stehen bei

Zimmertemperatur scheidet die alkoholische Lösung wenig Öl. Die in Alkohol lösliche Fraktion wird unter vermindertem Druck konzentriert. Zu dem zurückbleibenden festen Körper fügt man 15 ccm Benzol und die wenigen in Benzol unlöslichen Körperchen abfiltriert. Das benzolische Filtrat wird unter vermindertem Druck konzentriert. Man erhält 1.0 g kristall-ähnliche Körperchen vom Schmp. 105~110°C.

Anal. Gef.: C, 69.9; H, 5.7; -OCH_3, 12.5*. Ber. für $C_{23}H_{22}O_6$: C, 70.0; H, 5.6; -OCH_3, 15.8%.

Die Chromatographische Reinigung war effektivlos. Das aus dem Alkohol abgetrennte Öl lieferte beim Trocknen fast farblose non-kristallinische Körperchen vom Schmp. 195~200°C.

* Da diese Verbindung bei der Mikro-OCH_3-Analyse klumpig wurde, war die Entstehung des Methyliodids unvollständig, daher sind diese OCH_3-Werte etwas nieder.

Anal. Gef.: C, 67.36; H, 5.5; -OCH_3, 8.9*. Ber. für $C_{22}H_{20}O_6$: C, 69.5; H, 5.30; -OCH_3, 8.2%.

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Dielectric Constant of Liquid Consisting of Anisotropic Molecules

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Recently we have derived a formula for the internal field of polar liquid consisting of isotropic spherical molecules[1].

Our idea is based upon the classical electrostatics of continuous medium. Accordingly, the internal field is expressed as follows:

$$\vec{F}=\vec{E}-\vec{E}_s \tag{1}$$

where $\vec{F}$ is the internal field, $\vec{E}$ the electric field and $\vec{E}_s$ the self-field of a molecule. If the self-field is assumed to be dipolar,

$$\vec{E}_s=-\frac{4\pi}{3}\vec{p} \tag{2}$$

where $\vec{p}$ is the dipolar density.

We have assumed that p is the momentary dipolar density, i. e.;

$$\vec{p}=\frac{\vec{\mu}}{v} \tag{3}$$

where $\vec{\mu}$ is the momentary electric moment of the molecule, and v is the volume of the molecule.

1) M. Yasumi and H. Komooka, This Bulletin, **29**, 407 (1956).

$$\vec{\mu}=\vec{\mu}_0+\alpha\vec{F} \tag{4}$$

$\vec{\mu}_0$ is the permanent moment and α is the polarizability of the molecule.

For the liquid consisting of isotropic spherical molecules, the final expression for the internal field is as follows:

$$\vec{F}=\frac{n^2+2}{3}\left(\frac{\vec{\mu}_0}{a^3}+\vec{E}\right) \tag{5}$$

n denotes the (isotropic) refractive index and a is the radius of the spherical molecule.

On the other hand, Debye's internal field is readily obtained from Eqs. 1 and 2, if we assume that the dipolar density is the macroscopic one; i.e.,

$$\vec{p}=\frac{\varepsilon-1}{4\pi}\vec{E} \tag{6}$$

Using (6) and (2), Debye's internal field has the following expression.

$$\vec{F}=\frac{\varepsilon+2}{3}\vec{E} \tag{7}$$

It is our opinion that in calculating the internal field the dipolar density must be taken as the momentary one and not to be taken as the statistical one, because according to the definition the concept of the internal

field is referred to the molecule in the momentary state and is not referred to the molecule in the statistical state.

Assuming our expression for the internal field, the formula for the dielectric constant of polar liquid is readily derived and has the following expression:

$$\varepsilon-n^2=\frac{4\pi}{V}\left(\frac{n^2+2}{3}\right)^3\frac{\mu_0^2}{3kT} \tag{8}$$

This relation is closely related to the empirical relation of Wyman[2].

In spite of the simplified assumption, our equation 8 can fairly explain the experimental facts.

However, if we compare the experimental data with our equation 8 in detail, we can see that the degree of coincidence seems to depend on the chemical structure of the molecule forming a liquid.

On the other hand, most of the real molecules, especially polar molecules are not to be assumed to have spherical shapes and isotropic polarizabilities in general.

In this paper, we extend our previous theory to the case when a molecule has the shape of an ellipsoid and an anisotropic polarizability.

Formula for the Internal Field and the Dielectric Constant

We assume that the molecule forming a liquid has an anisotropic polarizability and a shape of ellipsoid.

We assume that the directions of the three principal axes of the ellipsoid are coincident with the directions of the coordinate axes (x_1, x_2, x_3).

The directions of the principal axes of the polarizability ellipsoid are not the same as those of the ellipsoid determining the molecular shape in general. However, we assume that these two sets of directions are coincident.

Let the lengths of the principal axes of the ellipsoid be $2a_1$, $2a_2$ and $2a_3$ respectively.

The dipolar density $\vec{p}$ of the liquid is represented as follows:

$$\vec{p}=\frac{\vec{\mu}}{v}=\frac{\vec{\mu}}{\frac{4\pi}{3}a_1a_2a_3} \tag{9}$$

The electride field $\vec{E}$ at a point of the liquid is resolved into two parts, i. e. the internal field $\vec{F}$ and the self-field $\vec{E}_s$.

$$\vec{E}=\vec{F}+\vec{E}_s \tag{10}$$

The component of the self-field of the ellipsoid along the direction of a principal axis x_i is expressed as[3];

$$E_{si}=-\varphi_i p_i \tag{11}$$

where

$$\varphi_i=2\pi a_1a_2a_3\int_0^\infty\frac{du}{(a_i^2+u)\sqrt{(a_1^2+u)(a_2^2+u)(a_3^2+u)}} \tag{12}$$

Accordingly, the component of the internal field $\vec{F}$ is represented as:

$$F_i=E_i+\varphi_i p_i \tag{13}$$

On the other hand, the total dipole moment of the molecule consists of the permanent dipole moment and the induced dipole moment.

$$\mu_i=\mu_{0i}+\alpha_i F_i \tag{14}$$

where α_i stands for the component of the polarizability tensor along the direction of the principal axis x_i[4].

From the Eqs. 9, 13 and 14,

$$F_i=\left(1-\frac{\varphi_i\alpha_i}{v}\right)^{-1}\left(E_i+\frac{\varphi_i\mu_{0i}}{v}\right) \tag{15}$$

If the number of the molecules in 1cc. of the liquid is denoted by N_c, then

$$1=N_cv \tag{16}$$

and

$$\begin{aligned}F_i&=(1-N_c\varphi_i\alpha_i)^{-1}(E_i+N_c\varphi_i\mu_{0i})\\&=\gamma_i(E_i+N_c\varphi_i\mu_{0i})\end{aligned} \tag{17}$$

The component of the total dipole moment of the molecule is expressed as:

$$\mu_i=\gamma_i(\alpha_iE_i+\mu_{0i}) \tag{18}$$

The component of $\vec{\mu}$ along the direcion of $\vec{E}$ is denoted by μ_E, and the statistical mean value of μ_E is denoted by $\langle\mu_E\rangle$. Assuming Boltzmann statistics, we have

$$\langle\mu_E\rangle=\int\mu_E\cdot e^{-U/kT}d\Omega\Big/\int e^{-U/kT}d\Omega \tag{19}$$

where U is the potential energy of the dipole under the influence of the electric field and $d\Omega$ is an elementary solid angle.

U has the following expression;

$$U=-\left\{\frac{1}{2}\sum\alpha_iF_i^2+\sum\mu_{0i}F_i\right\} \tag{20}$$

2) J. Wyman, *J. Am. Chem. Soc.*, **58**, 1482 (1936).

3) e. g. Stratton, "Electromagnetic Theory", McGraw-Hill Book Company, Inc., 1st Ed. (1941), pp. 207-213, 257.

4) φ and α are tensor quantities. However, in our case when they are diagonalized, only diagonal elements (φ_1, φ_2, φ_3) (α_1, α_2, α_3) are necessary.

and

$$\mu_E=\sum\mu_i\frac{E_i}{E}=\sum\gamma_i(\alpha_iE_i+\mu_{0i})\frac{E_i}{E} \quad (21)$$

Inserting 20 and 21 in 19 and making a simple calculation, we have;

$$<\mu_E>=\left\{\frac{\sum\alpha_i\gamma_i}{3}+\frac{\sum\mu_{0i}^2\gamma_i^3}{3kT}\right\}E \quad (22)$$

In this calculation $e^{-U_i/kT}$ is expanded in the power series of E_i, and only the terms proportional to E_i are retained.

The dielectric constant ε is related to $<\mu_E>$ by the following equation:

$$(\varepsilon-1)E=4\pi N_c<\mu_E> \quad (23)$$

Accordingly, we have

$$\varepsilon-1=4\pi N_c\left\{\frac{\sum\alpha_i\gamma_i}{3}+\frac{\sum\mu_{0i}^2\gamma_i^3}{3kT}\right\} \quad (24)$$

Consider, for a while, a non-polar liquid.

The refractive index of the liquid may be denoted by n. Then

$$n^2-1=4\pi N_c\frac{\sum\alpha_i\gamma_i}{3} \quad (25)$$

We define the quantity n_i by the following equation;

$$n_i^2-1=4\pi N_c\alpha_i\gamma_i \quad (26)$$

n_i may represent the refractive index of the molecule along the direction of the principal axis x_i.

From the Eqs. 25 and 26, we obtain

$$n^2=\frac{1}{3}\sum n_i^2 \quad (27)$$

It must be noticed that according to Lorentz-Lorenz field,

$$\frac{n^2-1}{n^2+2}=\frac{1}{3}\sum\frac{n_i^2-1}{n_i^2+2} \quad (28)$$

in contrast to our equation (27).

The equation 24 is transformed to the following form;

$$\varepsilon=\frac{\sum n_i^2}{3}+4\pi N_c\frac{\sum\mu_{0i}^2\gamma_i^3}{3kT} \quad (29)$$

In the cases of simple molecules, it may be assumed that the direction of the dipole moment coincides with one of the directions of the principal axes of the molecular ellipsoid. We choose the direction of the axis a_1, as the direction of the dipole moment.

In this case, the equation 29 reduces to

$$\varepsilon=\frac{\sum n_i^2}{3}+4\pi N_c\frac{\gamma_1^3\mu_0^2}{3kT} \quad (30)$$

According to J. Wyman[2] we define the quantity $\bar{p}$ by the following equation[5]:

$$\bar{p}=\frac{4\pi}{3}N_c\left\{\frac{\sum\alpha_i}{3}+\frac{\mu_0^2}{3kT}\right\} \quad (31)$$

then

$$\varepsilon+\frac{4\pi N_c}{3}\left\{\sum\alpha_i(\gamma_i^3-\gamma_i)\right\}-1=3\gamma_1^3\bar{p} \quad (32)$$

The equation 32 corresponds to Wyman's empirical relation[2]

$$\varepsilon+1=K_w\bar{p} \quad (33)$$

K_w represents a constant, amounting to 8.5 for most of normal liquids.

The quantity $3\gamma_1^3$ in our equation 32 which corresponds to K_w is slightly dependent on temperature, but practically is constant in the limited range of temperature[1].

Our present theory can treat the gaseous state if we take v appearing in the equation 9 as the volume portioned to one molecule. The form of the space occupied by this volume is assumed to be an ellipsoid confocal to the molecular ellipsoid.

In the gaseous state $N_c\alpha_i$ is much less than unity so the value of γ_i approaches to 1.

The equation (32) reduces to

$$\varepsilon-1=4\pi N_c\left\{\frac{\sum\alpha_i}{3}+\frac{\mu_0^2}{3kT}\right\} \quad (34)$$

The equation 34 coincides with the Debye's equation in the limiting case of $\varepsilon-1\ll1$.

Comparison of Our Formula with Experiments

In order to compare the value calculated with our theoretical formula the Eq. 29 or the Eq. 30 with the experimental value, we must know the value of permanent dipole moment, that of the component of polarizability and that of the molecular dimension.

a) The value of the permanent dipole moment. We take as the value of the permanent dipole moment, the value determined by the experiment of Stark effect in micro-wave spectroscopy.

However, in the case when this value is not available, the value determined by the measurement of the dielectric constant in the gaseous state is used.

b) The value of the component of polarizability. Two factors contribute to

5) In our previous paper[1], we define

$$\bar{p}=\frac{4\pi}{3}N_c\frac{\mu_0^2}{3kT}$$

However in the Wyman's original paper[2], $\bar{p}$ is defined as in this paper.

the polarizability of a molecule, i. e., the electronic polarization and the atomic polarization.

To determine the value of the component of polarizability, the experimental result of refraction, that of depolarization of polarized light, and that of Kerr effect, should be known.

The latter phenomenon concerns both the electronic polarization and the atomic polarization. On the other hand, the two other phenomena concern only the electronic polarization.

We use as the value of component of polarizability the value referred to in the literature of Stuart for the gaseous state[6] and that of Le Fèvre for the solution[7], when the datum for the gaseous state is not available.

This value does not include the contribution from the atomic polarization.

c) Moreover, we need the value of the molecular dimension. We use as the values of the interatomic distances and the values of valence bond angles the values determined by the experiments of electron diffraction or of micro-wave spectroscopy.

As the dimension of atomic size we use the usual van der Waals' radii[8].

From these values we construct a molecular model. Then we approximate a molecule as an ellipsoid, and determine the lengths of the principal axes. They are denoted by $2a_1$, $2a_2$ and $2a_3$, respectively. The direction of axis a_1 is assumed to be the same as that of the dipole moment.

A symmetrical top molecule can be approximated as a spheroid. In this case the parameter which determines the shape of the spheroid is only one. (i. e., the ratio of axes $a_2/a_1=a_3/a_1$).

We choose the value of the parameter in order to fit the experimental values of dielectric constant, and compare this value with the obtained from the geometrical configuration.

In some cases, we also calculate the value of dielectric constant with our formula taking as the value of axial ratio the value determined with the molecular model.

In the case of a general ellipsoid two parameters (i. e. a_2/a_1 and a_3/a_1) are necessary. In this case we use the values of the parameters determined from the geometrical configuration. We calculate the value of dielectric constant with our equation using these values and compare them with the experimental one.

Our assumption that a molecule may be approximated as an ellipsoid may not hold strictly.

In our calculation, we assume that the ratio of the lengths of the axes of the ellipsoid is independent of the temperature. Strictly saying, this assumption is not correct.

However, in the limited range of temperature, at which the liquid state exists, this assumption may be used without serious error.

For about thirty substances, the value of dielectric constant calculated with our formula is compared with the experimental one. As shown in the following tables the coincidence is strikingly excellent.

For most of the symmetrical top molecules the error is within a small percentage and for most of the asymmetrical top molecules the error is within 10 per cent.

The exceptions are revealed in the cases of methyl fluoride, nitromethane, nitrobenzene and diethyl ether.

In the following, some remarks are made on the individual cases.

1) Non-polar Liquid

For the non-polar liquid, our formula becomes coincident with Lorentz-Lorenz formula, provided that the molecule has a spherical shape and an isotropic polarizability[1]. However, if the molecule forming a liquid has an ellipsoidal shape and an anisotropic polarizability, our equation 25 does not coincide with that of Lorentz and Lorenz.

For benzene and carbon dioxide, we can not determine whether the Lorentz-Lorenz formula or our formula fit the experimental results.

For carbon disulfide it is recognized that the better agreement between the experimental value and the theoretical value is achieved if we calculate with our formula instead of the Lorentz-Lorenz formula.

Moreover the value of the ratio of the axes ($a_2/a_1=a_3/a_1$) obtained with our formla using the experimental results, is 0.5 which is in agreement with the geometrical value 0.54.

The considerable discrepancy between the experimental value and the theoretical

6) H. A. Stuart, Landolt-Börnstein Tabellen, I. Band (1951) 510, 512.

7) C. G. Le Fèvre and R. J. W. Le Fèvre, *Reviews of Pure and Applied Chemistry*, 5, 261-318 (1955).

8) L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press 1st. ed. (1939).

value calculated with Lorentz-Lorenz formula exists for the liquid state under high pressure. Moreover, the discrepancy is systematic (i.e., the higher the pressure, the greater the discrepancy).

It is striking that in this case the value calculated with our formula is in excellent agreement with the experimental one.

2) Symmetrical Top Molecule

a) Derivatives of methane

For methyl chloride and methyl bromide the theoretical value is fairly in agreement with the experimental one. The assumed ratio of the axes for methyl chloride is 0.75 (if the Stuart's data for Kerr effect are used) or 0.85 (if the Le Fèvre's data are used). The geometrical value is 0.71.

For methyl bromide the same order of agreement is recognized.

For methyl iodide a somewhat smaller value for the ratio of axes (0.45) is assumed in order to fit the experimental result. The value of the ratio of the axes obtained with the molecular model is 0.64.

For methyl fluoride the value of dielectric constant in the liquid state under high pressure is compared with the value calculated with our formula. If we assume 1.7 as the value of the ratio of the axes which corresponds to an oblate spheroid, the calculated value is in excellent agreement with the experimental one over the wide range of temperature. On the other hand, methyl fluoride has a shape of a prolate spheroid whose axial ratio is 0.85.

The reason why the value of the axial ratio calculated from the value of dielectric constant is inconsistent with the value calculated with the molecualr model is as yet obscure.

b) Other symmetrical top molecules

In the case of acetonitrile, *tert*-butyl chloride and chloroform our theory may be regarded as satisfactory.

3) Asymmetrical Top Molecule

As stated above, as the value of the axial ratio the value determined with the molecular model is used.

a) Nitromethane

The calculated value of dielectric constant is considerably smaller than the experimental one.

b) Methylene chloride.

The agreement is satisfactory.

c) Diethyl ether

The molecular shape of diethyl ether is as yet not determined completely. In table 16 the values of dielectric constant calculated with our formula using various values of axial ratio are shown, and compared with the experimental value.

The planar zig-zag form does not fit. The oblate spheroid whose axial ratio is 0.5 fit to the experimental results very well[9].

d) Other ethers

For dimethyl ether our theory can explain the experimental results quite satisfactorily if we use as the values of axial ratios the values determined with the molecular model.

For *n*-propyl ether, it seems that the zig-zag model is suitable. However, the lack of complete data prevents us from furfher discussion.

e) Paraldehyde

The molecular model is assumed to be the chair-form. This substance has the great atomic polarization. Accordingly we have taken into account the atomic polarization[10].

f) Acetone

The agreement of theoretical value with the experimental one is fairly satisfactory if we use as the value of the axial ratio the ratio determined with the molecular model.

g) Other ketones

In these cases, the value of dipole moment is assumed to be the same as that of acetone. The molecular forms are assumed to be planar zig-zag forms. If other suitable molecular models are assumed, better agreements would be obtained.

h) Derivatives of benzene, pyridine and quinoline

Except nitrobenzene, the calculated value of the dielectric constant is considerably in agreement with the experimental one, if we use as the values of the axial ratios the values determined with the molecular model. Nitrobenzene is assumed to have a coplanar molecular shape.

For nitrobenzene, the calculated value is considerably smaller than the experimental one, as in the case of nitromethane.

Appendix

Evaluation of φ_i. Let the lengths of three

9) On the other hand, the zig-zag model fits the experimental result of the Kerr effect when our internal field is used. Detailed discussion will appear in the following paper.

10) We define the quantity f as follows;

$$\frac{P_E+P_A}{P_E}=\frac{45.2}{33.1}=f$$

where P_E and P_A stand for the electronic and the atomic polarization respectively. In the calculation of the dielectric constant, $f\alpha_i$ is used instead of α_i.

principal axes of an ellipsoid be 2a, 2b and 2c respecti ely, and $a \geqq b \geqq c$.

φ_i's are represented as follows:[11]

$$\varphi_a = \frac{4\pi \frac{b}{a}\frac{c}{a}}{\left\{1-\left(\frac{c}{a}\right)^2\right\}^{3/2}} \frac{F(k,\rho)-E(k,\rho)}{k^2}$$

$$\varphi_b = \frac{4\pi \frac{b}{a}\frac{c}{a}}{\left\{1-\left(\frac{c}{a}\right)^2\right\}^{3/2}} \frac{1}{k'^2}\left\{\frac{E(k,\rho)-k'^2F(k,\rho)}{k^2} - \frac{\frac{c}{a}\sqrt{1-\left(\frac{c}{a}\right)^2}}{\frac{b}{a}}\right\}$$

$$\varphi_c = \frac{4\pi \frac{b}{a}\frac{c}{a}}{\left\{1-\left(\frac{c}{a}\right)^2\right\}^{3/2}} \frac{1}{k'^2}\left\{\frac{b}{a}\tan\rho - E(k,\rho)\right\}$$

where

$$k^2 = \frac{1-\left(\frac{b}{a}\right)^2}{1-\left(\frac{c}{a}\right)^2}$$

$$k'^2 = 1-k^2$$

$$\sin^2\rho = 1-\left(\frac{c}{a}\right)^2$$

$$F(k,\rho) = \int_0^\rho \frac{\mathrm{d}\theta}{\sqrt{1-k^2\sin^2\theta}}$$

$$E(k,\rho) = \int_0^\rho \sqrt{1-k^2\sin^2\theta}\,\mathrm{d}\theta$$

i. e., $F(k,\rho)$ and $E(k,\rho)$ represent the elliptic integral of first kind and that of second kind respectively. The numerical values of each are shown in the numerical tables[12].

In the case of sphere,

$$\varphi_a = \varphi_b = \varphi_c = \frac{4\pi}{3}$$

In the case of spheroid:

i) $a = b > c$

if we define as:

$$e^2 = 1-\left(\frac{c}{a}\right)^2$$

then

$$\frac{\varphi_c}{4\pi} = \frac{1}{e^2} - \frac{(1-e^2)^{1/2}\sin^{-1}e}{e^3}$$

and

$$\varphi_a = \varphi_b = 2\pi(1-\varphi_c)$$

ii) $a > b = c$

if we define as:

$$e^2 = 1-\left(\frac{b}{a}\right)^2$$

then

$$\varphi_a = 4\pi\left(\frac{1}{e^2}-1\right)\left(\frac{1}{2e}\ln\frac{1+e}{1-e}-1\right)$$

and

$$\varphi_b = \varphi_c = 2\pi(1-\varphi_a)$$

11) W. Magnus and F. Oberbethinger, "Formel und Sätze für die Speziellen Funktionen der Mathematischen Physik", (1948) Springer-Verlag. p. 136.

12) Marcell Boll, "Tables Numeriques Universelles", 1947.

Summary

Our previous theory of dielectric constant of liquid consisting of spherical molecules having an isotropic polarizability is extended to the case when the molecule has an ellipsoidal shape and an anisotropic polarizability.

The theory is compared with experimental results for about thirty substances. The coincidence is quite satisfactory with few exceptions. For non-polar substance, better agreement between the experimental value and the theoretical value is achieved if we use our formula instead of the Lorentz-Lorenz formula.

We are grateful to Professor San-ichiro Mizushima for his kind encouragement throughout this work and to Professor Akira Kotera for his kind advice. Our thanks are also due to the Ministry of Education for a grant in aid of this research.

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Phase Relationship in the System $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$—SiO_2

By Toshiyuki SATA

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The ternary system $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$—SiO_2 is of great importance in considering the compositions of the calcium-magnesium phosphatic fertilizer (or fused phosphatic fertilizer), and of bone ash magnesia porcelain. The author studied this equilibrium as a partial system of the ternary system $3CaO \cdot P_2O_5$—MgO—SiO_2. The equilibrium phase diagrams in this system have never before been presented.

Kiyoura and Sata[1,2] presented in 1953 the softening and melting diagrams of the system phosphate rocks-dunite-quartzite, and showed the most suitable composition for the fused phosphatic fertilizer as the one with the lowest softening and melting temperature regions in these diagrams. This equilibrium study is an extension of these investigations.

Experimental Procedure

Batches of selected compositions in the system $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$—SiO_2 were held at constant temperatures and quenched in water. Thenceforth the equilibrium phases found therein were determined by microscopic and X-ray examination.

Tricalcium phosphate ($3CaO \cdot P_2O_5$), magnesium metasilicate ($MgO \cdot SiO_2$) and silica (SiO_2) were used as raw materials. The first was prepared by the reaction of calcium carbonate with phosphoric acid or dicalcium phosphate ($2CaO \cdot P_2O_5$) with calcium carbonate at 1350°C. The second was prepared by calcining the mixture of magnesia and silica at 1300°C. The silica gel fired at 1200°C was used as SiO_2 raw material. After weighing, the batches were thoroughly mixed in an agate mortar with some methyl alcohol until they were dried, and calcined in a platinum crucible at 1200°C. The sample was crushed and mixed again and then heated on a platinum plate at 1200—1500°C, followed by rapid cooling in air.

Two silicon carbide resistor furnaces were used for this equilibrium study, the one with an inner diameter of 40 mm. (up to 1450°C) and the other 25 mm. (up to 1550°C).

The samples in platinum envelopes (8×8 mm.) were suspended by platinum wire (0.5 mm., 200 mm. long) in the center of the furnace and quenched together with this wire in water after being held at a constant temperature (±1°C). A thermocouple of platinum-platinum rhodium (10%) was used, and calibrated against the melting point of silver, copper and diopside.

Quenched samples were powdered and examined by a polarization microscope in the usual way and by X-ray diffractometer. X-ray examinations were carried out adding silicon metal (99.9%) to the samples as the standard material with a scanning speed 2θ 1°/min. The accuracy in reading patterns was decided to be ±0.04° using pure magnesia, quartz and silicon.

Results

The System $3CaO \cdot P_2O_5$—SiO_2.—Three reports have been already published on this system, as listed in Table I.

TABLE I
PREVIOUS RESULTS ON THE SYSTEM $3CaO \cdot P_2O_5$—SiO_2

Investigater	Eutectic temp.	Eutectic composition SiO_2	Max. solid solubility of SiO_2 in C_3P*
	°C	%	%
Trömel[3] (1948)	1540	10	5
Pierre[4] (1956)	1555	6—8	4
Wojciechowska[5] (1956)	1535	7.5	2.5

* Abbreviations used throughout this paper; $C_3P = 3CaO \cdot P_2O_5$, $S = SiO_2$, $M = MgO$, $MS = MgO \cdot SiO_2$, $M_2S = 2MgO \cdot SiO_2$.

The present experiments were intended to check the above observations, particularly the presence of the solid solution of SiO_2 in α or β modification of $3CaO \cdot P_2O_5$ by X-ray diffraction method. The results are shown in Table II.

These facts probably show the difficulty of the transition from α to β form of tricalcium phosphate in slow cooling and no variance of its transition temperature.

1) R. Kiyoura and T. Sata, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **54**, 756 (1951).
2) R. Kiyoura and T. Sata, ibid., **56**, 666-8 (1953).
3) G. Trömel, H. J. Harkort and W. Hotop, *Z. anorg. allg. Chem.*, **256**, 253-72 (1948).
4) P. D. S. St Pierre, *J. Amer. Cer. Soc.*, **37**, (6) 243 (1954); **39**, (4) 147 (1956).
5) J. Wojciechowska, J. Berak and W. Trzebiatowskii, *Roczniki Chem.*, **30**, 743-56 (1956); *Chem. Abst.*, **51**, 2373a (1957).

TABLE II

QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$—SiO_2

No.	SiO_2 %	Temp. °C	Time hr.	Condition	Phases present by X-ray exam.		
					α-C_3P	β-C_3P	Cristbalite
185	2	1550	—	slow-cooled	very large	very small	—
		1530	1	quenched	α only	none	—
		1250	5	quenched	large	small	—
		1100	5	quenched	small	large	—
186	5	1550	—	slow-cooled	very large	very small	—
		1530	1	quenched	α only	none	—
		1250	5	quenched	large	small	—
		1200	5	quenched	small	large	—
194	10	1530	1	quenched	large	none	none
		1450	1	slow-cooled	large	none	small
23	40	1530	1	quenched	large	none	large
		1200	—	slow-cooled	large	small	large

TABLE III

QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$

No.	Composition		Holding		Phases present
	C_3P wt. %	MS	Temp. °C	Time min.	
6	75.5	24.5	1407	50	glass
			1317	30	β-C_3P, glass
			1282	60	β-C_3P, M_2S, glass
			1222	60	β-C_3P, M_2S, clinoenstatite
25	67.3	32.7	1337	60	glass
			1326	60	β-C_3P, glass
			1305	60	β-C_3P, M_2S, glass
26	64.0	36.0	1337	60	glass
			1323	60	M_2S, glass
			1260	80	β-C_3P, M_2S, glass
			1244	60	β-C_3P, M_2S, clinoenst.
15	60.7	39.3	1348	60	very small M_2S, glass
			1332	60	M_2S, glass
			1314	60	M_2S, (clinoenst.), glass
			1292	60	β-C_3P, M_2S, (clinoenst.) glass
			1267	60	β-C_3P, M_2S, (clinoenst.) small glass
			1240	50	all crystal
4	50.8	49.2	1407	80	small M_2S, glass
			1287	60	M_2S, glass
			1272	60	small C_3P, M_2S, glass
			1252	60	C_3P, M_2S, small glass
36	47.0	53.0	1274	60	M_2S, glass
			1258	60	C_3P, M_2S, glass
31	43.6	56.4	1289	60	M_2S, glass
			1262	60	β-C_3P, M_2S, glass
			1247	50	β-C_3P, M_2S, clinoenst.

The X-ray diffraction patterns of α and β tricalcium phosphate in fired specimens indicated no change from their original patterns, as given in Fig. 1. Therefore the solid solubility of silica in tricalcium phosphate $3CaO \cdot P_2O_5$ mentioned by preceding authors is thought to be doubtful by these X-ray examinations.

The System $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$.— The quenching runs for this binary system are listed in Table III. Fig. 2 shows the equilibrium diagram obtained from the quenching data. The eutectic of this pseudo-binary system is at 40% $3CaO \cdot P_2O_5$ and 60% $MgO \cdot SiO_2$, and 1246±3°C, these data being obtained in connection with

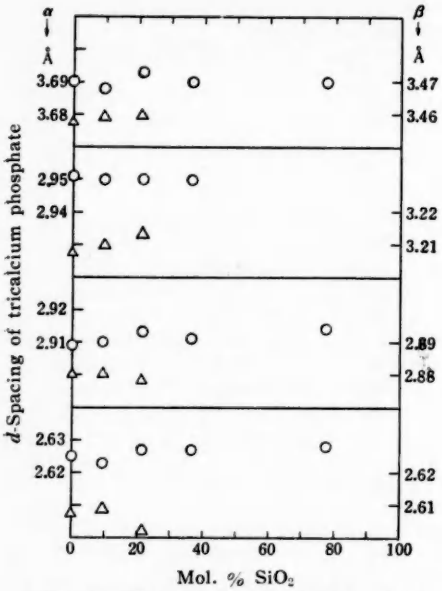

Fig. 1. The change of spacings of tricalcium phosphate.
○; α-$3CaO \cdot P_2O_5$, quenched from 1530°C.
△; β-$3CaO \cdot P_2O_5$, quenched from 1250°C.

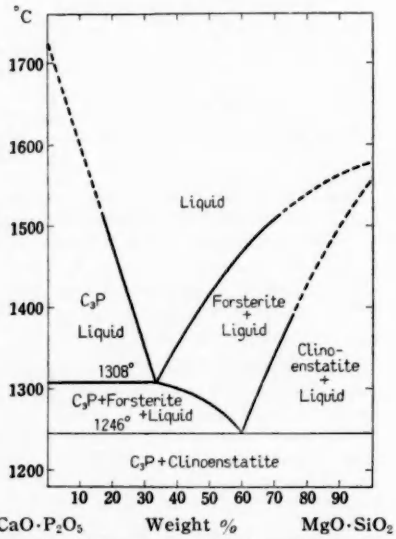

Fig. 2. The system tricalcium phosphate-magnesium metasilicate.

the result of the ternary system $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$—SiO_2. A minimum of the liquidus in the range from $3CaO \cdot P_2O_5$ to $2MgO \cdot SiO_2$ is at 33.5% $MgO \cdot SiO_2$ and at 1308°C.

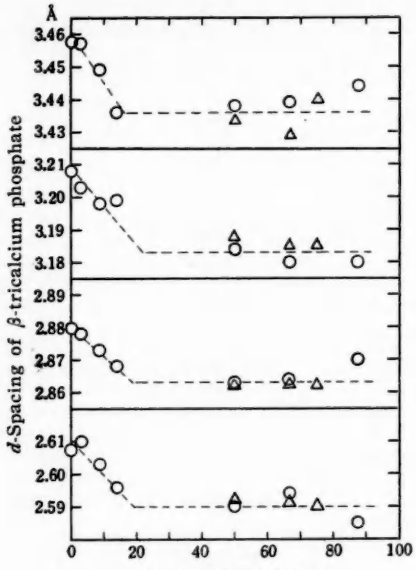

Fig. 3. The change of spacings of β-tricalcium phosphate.
○; quenched from 1250°C.
△; slow-cooled.

The presence of the pyroxene ($MgO \cdot SiO_2$) in quenched sample was chiefly determined by the microscopic examination of the powdered sample, however the X-ray diffraction patterns showed only β-tricalcium phosphate and forsterite, and no pyroxene line was found. It may owe to the difficulty of the equilibrium crystallization of magnesium metasilicate from this system. Only the β-modification, not α, of tricalcium phosphate appeared on X-ray diffraction patterns of all quenched samples at various temperatures, and there was no transition peak on the differential thermal analysis curves up to 1400°C. Thus it is to be concluded that β-tricalcium phosphate seemed to be stabilized at higher temperature over the transition point (1180°C) of pure tricalcium phosphate. The variation of the diffraction patterns of these β-form is indicated in Fig. 3, which shows the apparent solid solubility of 7±2 wt.% (19 mol.%) magnesium metasilicate in β-tricalcium phosphate at 1250°C. Nevertheless it is not yet clear whether tricalcium phosphate just dissolves magnesium metasilicate.

The System $3CaO \cdot P_2O_5$–$MgO \cdot SiO_2$–SiO_2. —The quenching data for this system are listed in Table IV, and the compositions of the mixtures are plotted in Fig. 4.

TABLE IV

QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$—$MgO \cdot SiO_2$—SiO_2

No.			Composition			Holding		Phases present
			C_3P	MgO	SiO_2	Temp. °C	Time min.	
			wt. %					
	No. 25	No. 23						
29	85	15	66.2	11.1	22.7	1332	60	C_3P, glass
						1232	45	C_3P, glass
						1208	60	C_3P, clinoenst., very small glass
37	80	20	65.8	10.5	23.7	1292	60	C_3P, glass
						1272	60	C_3P, small cristbl., glass
						1252	60	C_3P, cristbl., glass
27	70	30	65.1	9.2	25.7	1447	60	small cristbl., glass
						1352	60	cristbl., glass
						1324	60	cristbl., C_3P, glass
						1262	60	cristbl., C_3P, small glass
						1217	60	cristbl., C_3P, clinoenst.
	No. 15	No. 23						
48	90	10	60.6	14.2	25.2	1312	60	glass
						1282	50	small C_3P, glass
38	80	20	60.6	12.6	26.8	1312	60	glass
						1287	60	small C_3P, glass
32	70	30	60.5	11.0	28.5	1362	60	cristbl., glass
						1340	60	cristbl., tridymite, glass
						1290	60	cristbl., C_3P, glass
						1244	60	cristbl., C_3P, pyroxene*, glass
						1198	60	cristbl., C_3P, clinoenst.
	No. 4	No. 23						
44	80	20	52.6	15.8	31.6	1272	60	glass
						1264	60	M_2S, glass
						1255	50	C_3P, M_2S, glass
						1252	60	C_3P, M_2S, small glass
						1247	60	almost crystal
46	75	25	53.1	14.8	32.1	1252	60	small C_3P pyroxene* glass
45	70	30	53.5	13.8	32.7	1312	60	very small cristbl., glass
						1272	60	cristbl., glass
						1232	60	C_3P, cristbl., clinoenst.
	No. 31	No. 23						
42	90	10	45.3	20.3	34.4	1262	60	M_2S, small C_3P, glass
39	80	20	47.0	18.0	35.0	1282	60	very small M_2S, glass
						1262	60	M_2S, clinoenst., glass
						1254	60	almost crystal
47	75	25	47.7	17.0	35.3	1254	60	glass
						1247	60	clinoenst., glass
						1240	60	clinoenst., glass
						1232	60	clinoenst., C_3P, glass
						1224	60	all crystal
40	70	30	48.5	15.8	35.7	1272	60	glass
						1262	60	clinoenst., cristbl., glass
						1256	60	clinoenst., cristbl., glass
						1232	60	clinoenst., cristbl., C_3P
43	65	35	49.3	14.7	36.0	1447	60	glass
						1392	60	very small cristbl., glass
						1272	60	cristbl., glass
						1252	60	cristbl., clinoenst., glass
						1242	60	cristbl., clinoenst., C_3P, glass

41	60	40	50.2	13.6	36.2	1447	60	small cristbl., glass
						1332	60	cristbl., tridymite, glass
						1277	60	cristbl., tridymite, glass
						1262	40	cristbl., C_3P, clinoenst., glass
						1228	50	clinoenst., C_3P, cristbl.

* diopsidic pyroxene

Abbreviations; $C_3P=\beta$-$3CaO\cdot P_2O_5$, M_2S=Forsterite, Cristbl.=Cristobalite, Clinoenst.=Clinoenstatite.

These compositions are on the four lines joining No. 23 (60 C_3P—40 SiO_2) with No. 25, 15, 4, or 31 along the C_3P—MS. Fig. 4 was obtained as the phase diagram of this system in which two quintuple points occur, the one at 49% C_3P, 17% M, 34% S and 1246±3°C (alteration point), and the other at 50.5% C_3P, 15% M, 34.5% S and 1230±4°C (the ternary eutectic of the system C_3P—MS—S). It is to be noted that the tie line C_3P—MS may not intersect the boundary curve (alteration curve) between the clinoenstatite and forsterite fields. X-ray examinations of samples No. 42 and No. 47, quenched from 1200°C, gave the β-tricalcium phosphate and clinoenstatite patterns with faint forsterite in the case of the former.

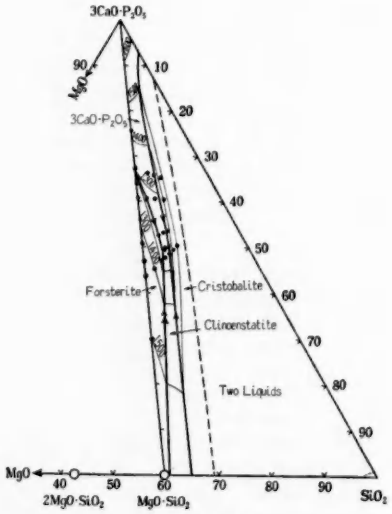

Fig. 4. The system tricalcium phosphate-magnesium metasilicate-silica.

Summary

The phase relationship in the system $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$—SiO_2 was investigated by the usual quenching method. In the partial system $3CaO\cdot P_2O_5$—SiO_2, the existence of solid solution and the change of the transition temperature of α—β tricalcium phosphate were not found by X-ray examinations.

The partial system $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$ is pseudo-binary, whose eutectic is at 1246°C and 40% $3CaO\cdot P_2O_5$. In this system, β-$3CaO\cdot P_2O_5$, always appeared in quenched samples, has a maximum solid solubility of 7±2% $MgO\cdot SiO_2$.

The system $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$—SiO_2 has two quintuple points, the one an alteration point and the other a ternary eutectic at 50.5% $3CaO\cdot P_2O_5$, 15.0% MgO, 34.5%SiO_2 that melts at 1230±4°C.

This system is of great importance to the manufacture of the fused phosphatic fertilizer and the bone ash magnesia porcelain. For instance, in this system, the lower liquidus groove lies at higher silica side along $3CaO\cdot P_2O_5$—$MgO\cdot SiO_2$, in accord with the results of cone fusion and melting point measurements already obtained by Kiyoura and Sata[1,2].

The author acknowledges the constant help and encouragement given by Professor Dr. R. Kiyoura, Tokyo Institute of Technology, and also much helpful advice supplied by Professor, Dr. H. Yamada and Assistant Professor S. Kawakubo, Tokyo Institute of Technology. This work was conducted as a part of a program to investigate the corrosion problems of various refractory bricks in the manufacture of fused phosphatic fertilizer.

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Polarographic Studies of Metallic Complexes. II.[1] *Isothiocyanato-ammine and Related Complexes of Chromium (III)*[2]

By Nobufumi MAKI, Yoichi SHIMURA and Ryutaro TSUCHIDA

(Received December 14, 1957)

There have been few reports on the relation between the half-wave potentials of chromium (III) complexes and their chemical structures, while some studies have been reported for the cobalt(III) complexes by several authors[1,3-6].

The present paper deals with the polarography of isothiocyanato-ammine series of chromium(III) complexes and the related compounds such as $[Cr\ en_3]Cl_3$, $[Cr\ en_2(NCS)_2]Cl$, or $[Cr\ en_2Cl_2]Cl$. The main purpose of this study is to examine the relationship between the polarographic stabilities of these complexes and their chemical structures. Furthermore, some examples of polarographic behavior of Reinecke's salt and *cis*-$[Cr\ en_2(NCS)_2]^+$ will be reported and discussed. These two salts are quite different from the other members of the chromium(III) isothiocyanato-ammine series from the viewpoint of their catalytic influences on the double wave of the oxygen dissolved in solution.

Experimental

Apparatus—A Heyrovsky-Shikata type polarograph, similar to that previously described[1], was employed to take the polarograms. An H-cell with a saturated calomel electrode was used. Two kinds of capillary were employed for measurements. One of them had an *m*-value of 5.828 mg./sec. and a drop time of 4.00 sec./drop and the other had an *m*-value of 33.661 mg./sec. and a drop time of 5.275 sec./drop. These characteristics of capillaries were measured in distilled water at the mercury height of 65 cm. with an open circuit. The cell temperature was maintained at 25±0.1°C by means of a water thermostat. The half-wave potentials were determined from the enlarged polarograms by "plotting method". The potential values were corrected for *iR*-drop by making use of the minimum value of the cell resistance. The reversibilities of the electrode reaction were tested by determining the slopes of $\log i/(i_d-i)$ vs. potential. Slopes of the log-plots indicated irreversible reduction throughout.

Material—The complex compounds studied were prepared by the methods described in literature[7-11] (the references are given in Tables I—II).

Each solution for the electrolysis was made freshly from the dry crystalline chromium(III) complexes before use and polarographic measurements were made as soon as possible after the removal of oxygen. The concentration of the solution was 0.001 F complex ion per litre. In order to remove the dissolved oxygen, a stream of nitrogen, which was purified from oxygen by means of an alkaline solution of pyrogallol, was bubbled through the cell solution for an hour prior to each electrolysis, preventing the evaporation. For the complexes which aquate easily in solution, such as *cis*-$[Cr\ en_2Cl_2]^+$, nitrogen was bubbled only half an hour and the polarographic runs were completed within ten minutes after the removal of oxygen. No maximum suppressor was used for the purpose of comparing the half-wave potentials of the complexes with one another. The presence of the maximum suppressor causes the lowering of the diffusion current and the shift of the half-wave potential to negative direction. The supporting electrolytes used were 0.1 F potassium chloride and 0.1 F or 1 F potassium thiocyanate.

Results and Discussion

The half-wave potentials of the isothiocyanato-ammine series of chromium(III) complexes are given in Table I. In the neutral and unbuffered solutions of 0.1 F potassium chloride and 0.1 F or 1 F potassium thiocyanate, all the compounds are reduced irreversibly in two steps at the dropping mercury electrode. As is shown in Table I, the half-wave potential

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TABLE I

HALF-WAVE POTENTIALS OF ISOTHIOCYANATO-AMMINE SERIES OF CHROMIUM(III) COMPLEXES

Complex	SUPPORTING ELECTROLYTE 0.1 F KCl		0.1 F KNCS		1 F KNCS	
	$E_{1/2}$ of 1st Wave	$E_{1/2}$ of 2nd Wave	$E_{1/2}$ of 1st Wave	$E_{1/2}$ of 2nd Wave	$E_{1/2}$ of 1st Wave	$E_{1/2}$ of 2nd Wave
$[Cr(NH_3)_6]Cl_3$[7]	−1.41	−1.65	——	——	——	——
$[Cr(NH_3)_5NCS](NCS)_2$[8]	−1.37	−1.65	−1.37	−1.64	−1.38	——*
$[Cr(NH_3)_4(NCS)_2]NCS$[9]	−1.34	−1.65	−1.34	−1.65	−1.34	——*
$NH_4[Cr(NH_3)_2(NCS)_4]$[10]	−1.31	−1.61	−1.07	——*	−1.23	——*
$K_3[Cr(NCS)_6]$[11]	——	——*	−0.74	——*	−0.79	——*

1) The concentration of the complexes: 0.001 F.
2) The characteristics of capillaries used: $m = 5.828$ mg./sec., $t = 4.00$ sec./drop.
3) * Maximum wave
4) Applied potential: V. vs. S.C.E.
5) Temperature: 25°C

TABLE II.

HALF-WAVE POTENTIALS OF THE CHROMIUM(III) COMPLEXES

Complex	$E_{1/2}$ of 1st Wave	$E_{1/2}$ of Aquated Complexes	$E_{1/2}$ of 2nd Wave
$[Cr(NH_3)_6]Cl_3$[7]	−1.41	No wave	——*
$[Cr\,en_3]Cl_3 \cdot 3.5\,H_2O$[14]	−1.38	No wave	——*
trans-$[Cr\,en_2(NCS)_2]Cl$[15]	−1.00	−1.30	——*
cis-$[Cr\,en_2(NCS)_2]Cl$[14]	−0.96	−1.30	——*
cis-$[Cr\,en_2Cl_2]Cl$[15]	−0.76	−1.28	——*

(V. vs. S.C.E.).

Supporting electrolyte: 0.1 F KCl.
Characteristics of capillaries used: $m = 33.661$ mg./sec., $t = 5.275$ sec./drop.
*Maximum wave.

of the first wave shifts to the direction of the more positive potential when the ammonia molecules of $[Cr(NH_3)_6]^{3+}$ are replaced by isothiocyanate ligands. While the half-wave potential of the second wave is always in close proximity to that of $[Cr(OH_2)_6]^{2+}$ ion ($E_{1/2} = -1.63$ V. vs. S.C.E. in 1 F potassium sulfate solution)[12]. Judging from these facts the first wave apparently represents the reduction of chromium(III) complexes to chromium (II) state, and the second represents the reduction to metallic state.

The height of the second wave is significantly greater than twice that of the first wave. The ratio of the wave heights increases with the decreasing concentration of the chromium(III) complexes. Therefore, the second wave is likely to include the "hydrolysis current" which was thoroughly studied by J. J. Lingane and R. L. Pecsok[13]. Thus the hydrogen ion from the hydrolysis of the complexes may contribute to the second diffusion current.

In the supporting electrolyte of 1 F potassium thiocyanate the second wave of these chromium(III) complexes have the maxima, which can not be suppressed in the presence of the high concentration of the usual surface active agents such as gelatin, methyl red, Triton-X 100* or Tween-80**.

The process of the reduction of $[Cr(NH_3)_6]^{3+}$ is considered as follows:

$$[Cr(NH_3)_6]^{3+} + e^- \rightarrow [Cr(NH_3)_6]^{2+}$$
$$[Cr(NH_3)_6]^{2+} + 6H_2O \rightarrow [Cr(OH_2)_6]^{2+} + 6NH_3$$
$$[Cr(OH_2)_6]^{2+} + 2e^- \rightarrow Cr + 6H_2O.$$

Similar mechanisms are applicable to the other chromium(III) complexes here studied. Table II shows the half-wave potentials of some chromium(III) complexes other than the isothiocyanato-ammine series.

For the complexes of $[Cr\,en_2X_2]^+$ type it is expected that they are easily aquated in solution. In fact, these complexes gave rise to the two distinct polarographic waves for the reduction step of chromium

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13) J. J. Lingane and R. L. Pecsok, *J. Am.* Chem. Soc. **71**, 425 (1949).
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15) C. L. Rollinson, J. C. Bailar, Jr. and J. P. McReynolds, "Inorganic Syntheses", Vol. 2, p. 200 (1946).
* Alkylated aryl polyether alcohol (Rohm & Haas Co. in U. S. A.).
** Polyoxyethylene sorbitan mono-oleate (Atlas Powder Co. in U. S. A.).

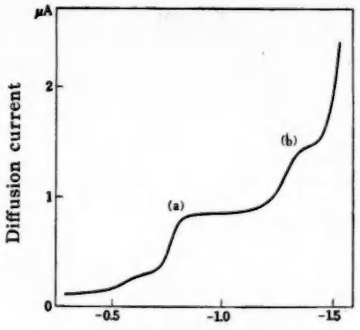

Fig. 1. The polarogram of *cis*-[Cr en_2Cl_2]Cl in 0.1 F KCl.
The concentration of the complex: 0.001 F.
a) The reduction wave of *cis*-[Cr en_2Cl_2]$^+$ to Cr(II) state.
b) The reduction wave of the aquated Cr(III) complexes to Cr(II) state.

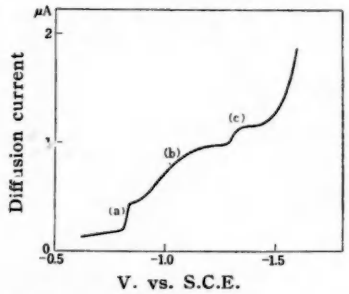

Fig. 2. The polarogram of *cis*-[Cr $en_2(NCS)_2$]Cl in 0.1 F KCl.
The concentration of the complex: 0.001 F.
a) The oxygen wave. (It was impossible to diminish the wave.)
b) The reduction wave of *cis*-[Cr $en_2(NCS)_2$]$^+$ to Cr(II) state.
c) The reduction wave of the aquated Cr(III) complexes to Cr(II) state.

(III)→chromium(II). Figs. 1 and 2 show the typical polarograms. This double wave is thought to be due to an aquation of the complexes. In the process of the aquation one or two of the coordinated negative radicals are replaced by water molecules, resulting in an equilibrium mixture of the aquated and the originial species. For instance,

trans-[Cr $en_2(NCS)_2$]$^+$ + H_2O →*trans*-[Cr $en_2(OH_2)NCS$]$^{2+}$ + NCS^-,

trans-[Cr $en_2(OH_2)NCS$]$^{2+}$ + H_2O →*trans*-[Cr $en_2(OH_2)_2$]$^{3+}$ + NCS^-.

Thus the first wave of the double wave represents the reduction of the original complex and the second that of the aquated species. This postulate is advanced for the following reason. For the *cis* and *trans* isomer of [Cr $en_2(NCS)_2$]$^+$, the half-wave potentials of the second of the double wave have the same values of −1.30 V. vs. S.C.E. within the experimental errors.

The diffusion current of the second waves increased with time. This evidently owes to the formation of the aquo-complexes. For instance, forty minutes after the preparation of the solution, the height of the second wave of [Cr en_2Cl_2]$^+$ is approximately three times as high as that of the second wave of *cis*- or *trans*-[Cr $en_2(NCS)_2$]$^+$. This means that *cis*-[Cr en_2Cl_2]$^+$ aquates more rapidly than *cis*- or *trans*-[Cr $en_2(NCS)_2$]$^+$.

For the benefit of comparing the half-wave potentials of the first wave with

TABLE III

THE HALF-WAVE POTENTIAL OF THE FIRST WAVE OF THE RELATED COMPLEXES OF Cr(III) AND Co(III)[a,1]

Cr(III) Complex	$E_{1/2}$
$[Cr(NH_3)_6]^{3+}$	−1.41
[Cr en_3]$^{3+}$	−1.38
$[Cr(NH_3)_4(NCS)_2]^+$	−1.34
cis-[Cr $en_2(NCS)_2$]$^+$	−0.94
trans-[Cr $en_2(NCS)_2$]$^+$	−1.00
Co(III) Complex[b]	$E_{1/2}$
$[Co(NH_3)_6]^{3+}$	−0.24
[Co en_3]$^{3+}$	−0.43

(V. vs. S.C.E.)

a) The supporting electrolyte: 0.1 F KCl.
b) The experimental conditions are almost the same as for the Cr(III) complexes except the temperature and the characteristics of the capillaries.

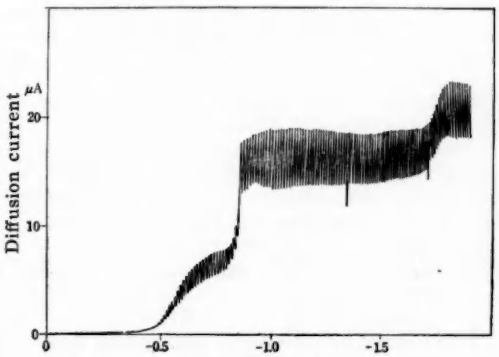

Fig. 3. The polarogram of the double wave of oxygen in the presence of 0.001 F $NH_4[Cr(NH_3)_2(NCS)_4]$ and 0.1 F KCl.

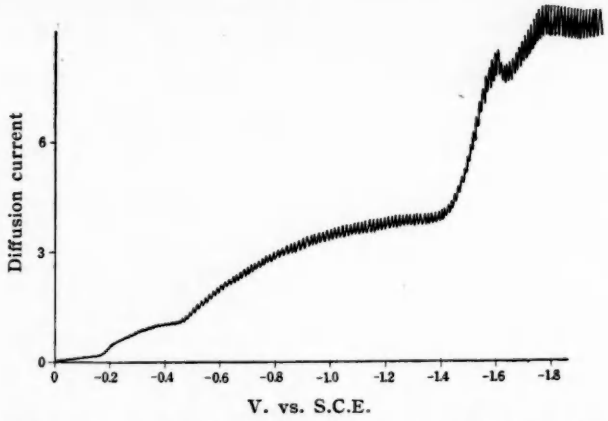

Fig. 4. The polarogram of 0.001 F $K_3[Cr(NCS)_6]$ in 0.1 F KCl. This polarogram was taken immediately after bubbling nitrogen through the solution for an hour.

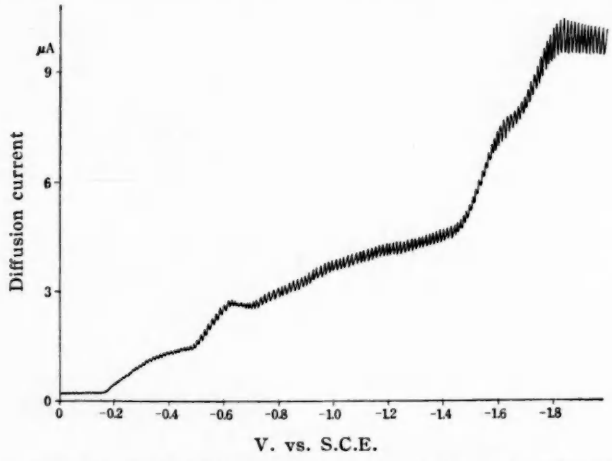

Fig. 5. The polarogram of 0.001 F $K_3[Cr(NCS)_6]$ in 0.1 F KCl. This polarogram was taken ten minutes after the polarographic run of Fig. 5 being completed. It was impossible to determine the half-wave potential of $K_3[Cr(NCS)_6]$ in 0.1 F KCl owing to the interference of the double wave of oxygen.

one another, a part of the data is picked up again here in Table III.

From the comparison of the half-wave potentials for the reduction step of chromium(III)→chromium(II) in the Tables I, II and III, it was found that the polarographic stabilities of the chromium(III) complexes increase in the following order of the ligands:

$$Cl^- < NCS^- < en < NH_3$$

In this series it should be noted that the order of ethylenediamine and ammonia is quite contrary to the order of these ligands for cobalt(III) complexes.

The fact that the *trans* isomer of $[Cr en_2(NCS)_2]^+$ has a slightly more negative half-wave potential than that of the corresponding *cis* isomer agrees with the results obtained by Holtzclaw et al.[3] in the several pairs of *cis* and *trans* isomers of cobalt(III) complexes.

The Peculiar Polarographic Behaviors of *cis*-$[Cr\ en_2(NCS)_2]Cl$ and Reinecke's Salt, $NH_4[Cr(NH_3)_2(NCS)_4]H\cdot_2O$. In the presence of 0.001 F $NH_4[Cr(NH_3)_2(NCS)_4]$ in 0.1 F potassium chloride solution, the first wave of oxygen dissolved in the solution shifted to the direction of negative potential and the wave forms of both the first and the second of the oxygen

double wave were extraordinarily modified. Fig. 3 shows the typical polarogram of the dissolved oxygen in the presence of Reinecke's salt. This polarogram was taken after bubbling oxygen into the solution for an hour. It seemed that the limiting current of the oxygen wave depends upon the concentration of oxygen dissolved in the solution. In open air the current value changed from 0.95μA at 25°C after expelling the dissolved oxygen to 8.10μA after saturating oxygen at 25°C. The half-wave potential of the first wave is −0.50 V. (vs. S.C.E.) and that of the second is −0.85 V. (vs. S.C.E) for the solution saturated with oxygen in the air (25°C).

Hexaisothiocyanato chromium(III) complex, $[Cr(NCS)_6]^{3-}$, also shows such kinds of polarographic behavior, though slightly. In the solution of 0.1 F potassium chloride the half-wave potential of the first wave of $[Cr(NCS)_6]^{3-}$ is near to that of the second wave of oxygen double wave and the two waves overlap with each other (Figs. 4 and 5).

No catalytic effects on the double wave of oxygen have been found in the other members of the isothiocyanato-ammine series of chromium(III) complexes. Fig: 6 shows the typical polarogam of the dissolved oxygen in the presence of

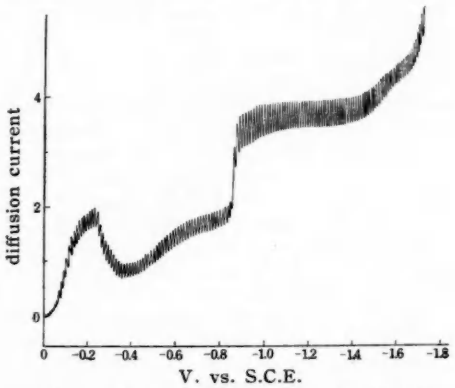

Fig. 6. The polarogram of the double wave of oxygen in the presence of 0.001 F *cis*-$[Cr\,en_2(NCS)_2]Cl$ and 0.1 F KCl.

0.001 F *cis*-$[Cr\,en_2(NCS)_2]Cl$ and of 0.1 F potassium chloride. The first wave of the oxygen double wave has a maximum and the second has the same wave-form and the same half-wave potential (−0.85 V. vs. S.C.E.) as in the case of the Reinecke's salt. The corresponding *trans* isomer, *trans*-$[Cr\,en_2(NCS)_2]Cl$, has never shown the catalytic effects on the oxygen waves.

It should be noted here that all the complexes which show the catalytic effects on the double wave of oxygen have two isothiocyanate ligands on *cis* positions in the coordinated sphere. Therefore, the fact that $[Cr(NH_3)_4(NCS)_2]^+$ did not show such polarographic behavior might be considered as a proof for the *trans* structure of the ion.

Summary

1. In neutral and unbuffered solution of 0.1 F potassium chloride, 0.1 F potassium thiocyanate, or 1 F potassium thiocyanate, the complex ion, $[Cr(NH_3)_n(NCS)_{6-n}]^{n-3}$ and $[Cr\,en_3]^{3+}$ were all reduced irreversibly in two steps at the dropping mercury electrode. The first diffusion current corresponds to the reduction, chromium(III) →chromium(II), and the second to the reduction, chromium(II)→chromium(0).

2. In the solution of 0.1 F potassium chloride, the polarograms of $[Cr\,en_2X_2]^+$ type complexes show three waves. Each of the first two waves, corresponding to a gain of one electron, represents the reduction of chromium(III) to chromium(II) and the last wave, corresponding to a gain of two electrons, represents the reduction to the metallic state. As regards the first two waves, the former wave represents the reduction of the original chromium(III) complexes to chromium(II) state and the latter represents the reduction of the aquated chromium(III) complexes to chromium(II) state.

3. In agreement with the results obtained for cobalt(III) complexes by Holtzclaw et al., the *trans* isomer of $[Cr\,en_2(NCS)_2]^+$ has a little more negative half-wave potential than the corresponding *cis*-form.

4. The polarographic stabilities of chromium(III) complexes increase in the following order of the ligands:

$$Cl^- < NCS^- < en < NH_3$$

5. The catalytic effects on the double wave of oxygen have been found for $[Cr(NH_3)_2(NCS)_4]^-$, $[Cr(NCS)_6]^{3-}$, or *cis*-$[Cr\,en_2(NCS)_2]^+$. Such special polarographic behavior was not found in the other chromium(III) complexes.

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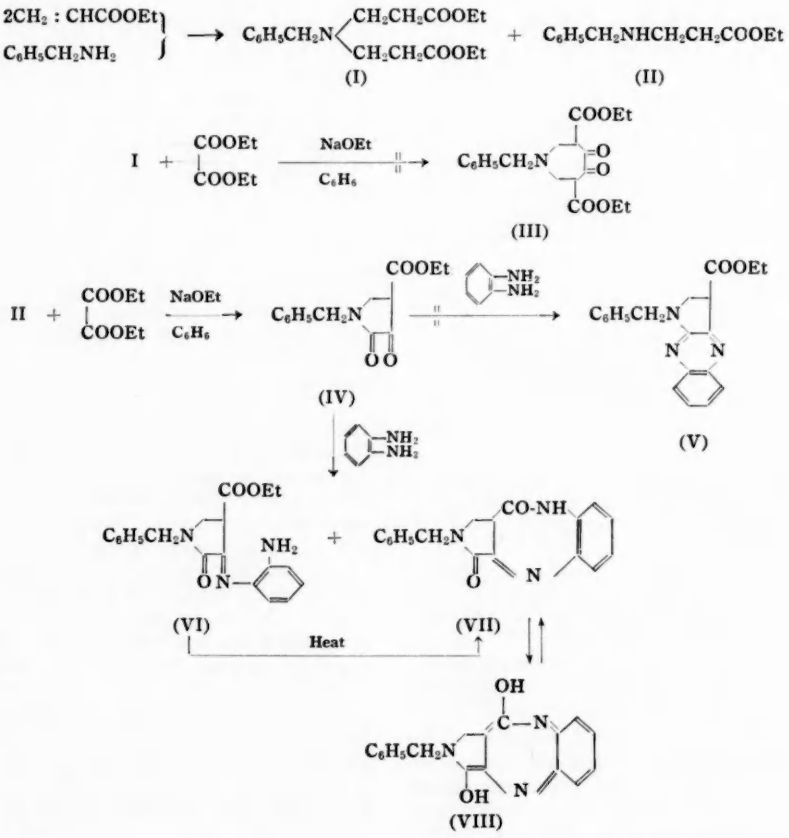
Studies on Seven-Membered Heterocyclic Compounds Containing Nitrogen. II. An Improved Synthesis of 1-Azacycloheptan-4-one and Its Related Compounds

By Shiro MOROSAWA

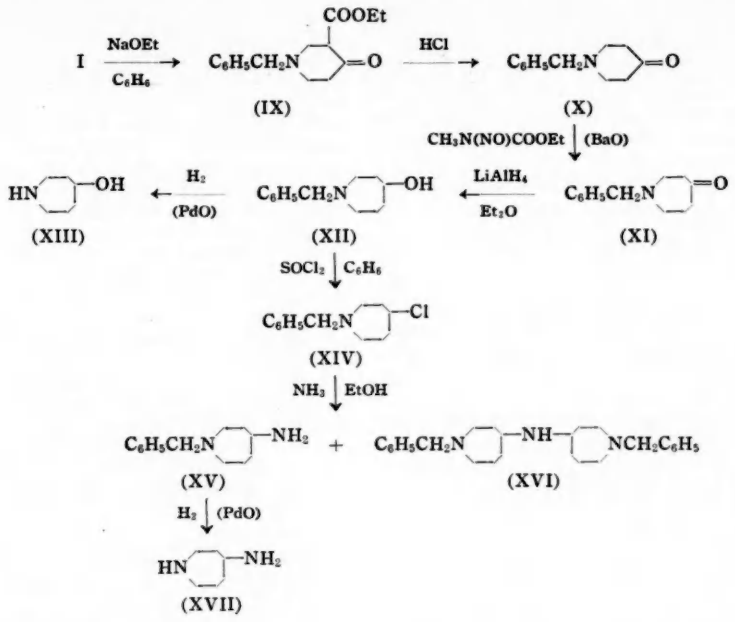
(Received January 30, 1958)

It was reported in the former paper[1] that 1-azacycloheptan-4-one (XI) was synthesized from ethyl *N*-benzyl-γ-(β-carbethoxyethylamino)-butyrate[2] by the Dieckmann condensation. The preparation of the butyrate, however, was so troublesome that the author tried to obtain XI by ring enlargement of 1-benzyl-4-piperidone (X) which prepared from *N,N*-bis-(β-carbethoxyethyl)-benzylamine (I) by the Dieckmann condensation.

The method of G. Stork and S. M. McElvain[3] was applied to the preparation of I, and a fraction of b. p. 200~210°C/0.5 mm. was obtained. The author tried at first to prepare azacycloheptane dione (III)



1) A. Yokoo and S. Morosawa, This Bulletin, **29**, 631 (1956).
2) A. Yokoo and S. Morosawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 599 (1956).
3) G. Stork and S. M. McElvain, *J. Am. Chem. Soc.*, **69**, 971 (1947).



from I and ethyl oxalate, and the fraction was heated with ethyl oxalate in the presence of sodium ethoxide in benzene. But unexpectedly, azacyclopentane dione (IV) was formed. IV was also obtained from ethyl oxalate and pure ethyl β-benzylaminopropionate (II)[3] which was prepared by the Stork and McElvain's method. It was assumed that possibly ethyl oxalate condensed with II which was previously contained in the fraction, or formed by decomposition of I during the heating. With *o*-phenylenediamine IV did not afford a compound of phenazine type (V) but two kinds of crystal; one was light yellow of m. p. 127~8°C and the other orange of m. p. 265~270°C (decomp.). They were revealed from their elementary analyses to have formulae VI and VII (or VIII), respectively. Infrared absorption spectrum of the latter crystals showed the absence of an ester and the primary amine, but because of a wide absorption band (1630~1680 cm.$^{-1}$) near the carbonyl and enol, it was not clearly determined which structure, VII or VIII, is preferable. VI was converted into VII by heating.

Some different boiling points have been reported for I[3,4], but as a result of the present study it was distilled out at 200~210°C/0.5 mm. along with ethyl acrylate which was detected by its faint odor; nitrosoation test with sodium nitrite for the distillate indicated the presence of a secondary amine II. On pyrolysis, the distillate began to decompose at about 197°C to yield ethanol and ethyl acrylate, leaving a residue which was distilled out at 165~210°C/0.65 mm. without indicating a constant boiling point.

From these experiments, it is obvious that I is apt to be affected by heating and can not be refined even by vacuum distillation. In the present study, therefore, the tertiary amine I was separated from the reaction mixture by removing the secondary amine II as a nitroso compound, in 65.5% yield. I thus obtained was possibly considered to be pure from its nitrogen analysis, and was also decomposed at about 197°C on pyrolysis. On heating with an equivalent amount of sodium ethoxide in dry benzene, I was converted into hydrochloride of 1-benzyl-3-carbethoxypiperid-4-one (IX)[4] of m.p. 175°C (decomp.) as colorless prisms in 82.5% yield, which by decarboxylation with hydrochloric acid gave 1-benzylpiperid-4-one (X)[5] as a colorless oil of b. p. 143~6°C/5 mm.

The ring enlargement of X was performed by the C. G. Overberger and A.

4) J. R. Thayer and S. M. McElvain, ibid., **49**, 2862 (1927).

5) G. Stork and S. M. McElvain, ibid., **68**, 1053 (1946).

Katchmann's method[6] who prepared 4-oxo-thiaepane from tetrahydro-1,4-thiapyrone and nitrosomethylurethane in the presence of barium oxide. In order to purify the crude product, this was dissolved in dry ether, and dry hydrogen chloride was passed through to precipitate it as a hydrochloride, which was recrystallized from methanol and ether. The melting point of the hydrochloride was not depressed on admixture with the one described in the former paper. Free base XI was regenerated from the hydrochloride with potassium carbonate, and gave 2,4-dinitrophenylhydrazone hydrochloride, which was also identified as the former one by mixed fusion.

Lithium aluminum hydride reduction of XI afforded 1-benzyl-1-azacycloheptan-4-ol (XII) as a colorless oil of b.p. 129°C/0.5 mm. in 95.5% yield, which on catalytic reduction with palladous oxide yielded 1-azacycloheptan-4-ol (XIII) as a hygroscopic colorless viscous oil of b.p. 82°C/0.5 mm. in 56.2% yield. XIII gave a picrolonate of m.p. 225°C (decomp.). With thionyl chloride, XII afforded 1-benzyl-4-chloro-1-azacycloheptane (XIV) as a hygroscopic colorless liquid of b.p. 104~5°C/0.3 mm. in 67.3% yield, which on standing gradually crystallized. Heating a mixture of XIV and absolute ethanol, saturated with ammonia at 0°C, in a sealed tube gave 4-amino-1-benzyl-1-azacycloheptane (XV) as a colorless oil of b.p. 105~6°C/0.4 mm. in 71% yield. Bis-(4-benzyl-4-azacycloheptyl)-amine (XVI) was also thereby obtained as a higher-boiling, light yellow viscous oil of b.p. 219~221°C/0.3 mm., which gave a picrolonate of m.p. 213°C (decomp.). XV gave a chloroaurate as yellow micro plates of m.p. 194°C(decomp.). Catalytic reduction of XV in the presence of palladous oxide as a catalyst afforded 4-amino-1-azacycloheptane (XVII) as a hygroscopic colorless oil of b.p. 80°C/10 mm., which on standing in the atmosphere gradually deposited white crystalline precipitates under fuming. XVII gave a chloroaurate of m.p. 209°C (decomp.) and a picrate of m.p. 224°C (decomp.).

Experimental

***N,N*-Bis-(β-carbethoxyethyl)-benzylamine (I).**—A mixture of 80 g. of benzylamine and 190 g. of ethyl acrylate was refluxed in an oil bath for 20 hr. After cooling, a mixture of 200 cc. of concentrated hydrochloric acid and 300 cc. of water was added and cooled to below 5°C in an ice-water bath, followed by the addition of 90 g. of solid sodium nitrite in small portions under agitation. After further agitation for 30 min., the mixture was extracted with a mixture of 200 cc. of benzene and 100 cc. of ether. The organic layer was extracted 8 times with each 200 cc. portion of 3 N hydrochloric acid and discarded. Aqueous layers were united and made alkaline by adding 650 g. of anhydrous sodium carbonate and extracted with a mixture of 200 cc. of benzene and 200 cc. of ether, then with that of 100 cc. of benzene and 100 cc. of ether. The extracts were united and washed with a diluted solution of sodium carbonate, and water and dried over calcium chloride. The solvent was distilled off on a water bath; the residue is further heated under reduced pressure until nothing had been distilled out. After that, the reduced pressure was held under heating on a water bath for another one hour, leaving 150 g. (65.5%) of an oily substance. (Found: N, 4.63%).

1-Benzyl-4-carbethoxy-1-azacyclopenta-2,3-dione (IV).—To a suspension of 3.1 g. of powdered sodium in 150 cc. of dry benzene was added 6 g. of absolute ethanol and heated with stirring to convert the sodium into sodium ethoxide. After cooling, a mixture of 13.8 g. of II (b.p. 133~5°C/2 mm.) and 10 g. of ethyl oxalate was added and allowed to stand overnight. In order to distill out 100 cc. of the azeotropic mixture of ethanol and benzene, the resulting mixture was heated in a water bath with stirring. The mixture in the reaction flask was washed with water and 2 N hydrochloric acid until the washing became acidic. The benzene solution was evaporated to a small volume. Crystals formed on standing were filtered, washed with water and recrystallized from ethanol to give 8 g. (46%) of colorless crystals, m.p. 133~4°C.

Anal. Found: C, 64.13; H, 5.86; N, 5.19. Calcd. for $C_{14}H_{15}O_4N$: C, 64.3; H, 5.76; N, 5.37%.

Compounds VI and VII.—A mixture of 1 g. of IV, 1 g. of *o*-phenylenediamine and 10 cc. of ethanol was refluxed on a water bath for 7 hr. Orange crystals formed were filtered and recrystallized from a large amount of ethanol to give 0.2 g. of orange plates (VII), m.p. 265~270°C (decomp.).

Anal. Found: C, 70.85; H, 5.19; N, 13.49. Calcd. for $C_{18}H_{13}O_2N_3$: C, 70.8; H, 4.93; N, 13.76%.

The filtrate of VII was evaporated and allowed to stand. Crystals formed were recrystallized twice from ethanol to yield 1.2 g. of light yellow crystals (VI), m.p. 127~8°C.

Anal. Found: C, 68.28; H, 6.27; N, 11.81. Calcd. for $C_{20}H_{21}O_3N_3$: C, 68.3; H, 5.98; N, 11.95%.

VII by heating VI.—After heating 0.5 g. of VI at 155~165°C in an oil bath for 5 hr., a small amount of ethanol was added, heated and decanted repeatedly. Remaining crystals were recrystallized from a large amount of benzene to

6) C. G. Overberger and A. Katchmann, ibid., **78**, 1967 (1956).

give 0.3 g. of orange crystals (VII).

1-Benzyl-3-carbethoxypiperid-4-one (IX) hydrochloride.—To a suspension of 7.5 g. of powdered sodium in 30 cc. of dry xylene were added 300 cc. of dry benzene and 17 cc. of absolute ethanol, and heated under stirring to convert the sodium into sodium ethoxide. After cooling, a solution of 100 g. of I in 180 cc. of dry benzene was added within 5 min. with stirring. After about 10~20 min., the resulting mixture became gel-like and could not be stirred; it was allowed to stand overnight. About 200 cc. of the solvent was distilled out by heating the mixture for 4 hr. After cooling, 100 cc. of water and 100 cc. of concentrated hydrochloric acid were added to deposit an oily matter, which gradually crystallized. After standing for 2 hr., the crystals were filtered, recrystallized from 40 cc. of ethanol and washed with a mixture of 25 cc. of ethanol and 25 cc. of ether to give 80 g. (82.5%) of IX hydrochloride as colorless prisms, m.p. 175°C (decomp.). (Found: C, 60.77; H, 7.02; N, 4.33%).

1-Benzylpiperid-4-one (X).—A mixture of 120 g. of IX hydrochloride, 400 cc. of concentrated hydrochloric acid and 350 cc. of water was refluxed for 3 hr. After cooling, the solution was evaporated to dryness under reduced pressure. The residue was dissolved in 50 cc. of water, and 100 g. of anhydrous potassium carbonate was added. Liberated oil was extracted 4 times with ether (100 cc., 100 cc., 50 cc. and 50 cc. respectively), and the combined ether extract was dried over potassium carbonate. Ether was removed and vacuum distillation gave 61 g. (70%) of a colorless oil, b. p. 143~6°C/5 mm. (Found: N, 7.24%).

X gave 2,4-dinitrophenylhydrazone hydrochloride as yellow prisms of m. p. 223°C (decomp.).

Anal. Found: N, 17.26. Calcd. for $C_{18}H_{19}O_4N_5 \cdot HCl$: N, 17.63%.

1-Benzyl-1-azacycloheptan-4-one (XI) by ring enlargement.—In a three-necked, round-bottomed flask, fitted with a Hershberg stirrer and a dropping funnel, 61 g. of X and 100 cc. of methanol were placed and cooled to −15°C in an ice-salt mixture. The stirring was started, and 45 g. of nitrosomethylurethane was added dropwise within 9 hr. During that time, 2 g. of barium oxide was added in small portions, and the temperature in the flask indicated about −5°C. After being kept overnight in the ice-salt mixture, the reaction mixture was filtered from any solid present, and the methanol was expelled under reduced pressure. The residue was dissolved in 400 cc. of ether and the undissolved polymethylene polymers were filtered off. Dry hydrogen chloride was passed through the ether to give a precipitate, which was separated by decantation, dried, recrystallized from 40 cc. of methanol and 20 cc. of ether and washed thrice with a mixture of 15 cc. of methanol and 15 cc. of ether to yield 28.3 g. of XI hydrochloride, m. p. 184~5°C (decomp.). Evaporation of the filtrate gave a further crop of crystals, which was recrystallized as before to give 3 g. of the substance, m. p. 184~5°C (decomp.). The total yield was 43.6%. The melting point of this hydrochloride was not depressed on admixture with that described in the former paper.

The hydrochloride was dissolved in 15 cc. of water and 40 g. of potassium carbonate was added. Oil thereby liberated was taken up in ether and dried over potassium carbonate. After removal of ether, vacuum distillation gave 24.8 g. (37.8%, based on X) of free base as a colorless oil, b. p. 129°C/0.5 mm.

2,4-Dinitrophenylhydrazone hydrochloride of m. p. 214°C (decomp.) derived from XI did not either depress the m. p. of the former one on mixed fusion. (Found: N, 16.60%).

1-Benzyl-1-azacycloheptan-4-ol (XII).—A solution of 11.1 g. of XI in 150 cc. of dry ether was added dropwise to 1.05 g. of lithium aluminum hydride suspended in 100 cc. of dry ether without cooling during 1 hr. under stirring, which was continued for 15 min. The excessive hydride was then decomposed by adding dropwise 19 cc. of water with stirring. Ether was decanted, dried over magnesium sulfate and removed by distillation. The residue was distilled to yield 10.7 g. (95.5%) of a colorless oil, b. p. 129°C/0.5 mm.

Anal. Found: C, 74.90; H, 9.46; N, 6.70. Calcd. for $C_{13}H_{19}ON$: C, 76.05; H, 9.33; N, 6.82%.

1-Azacycloheptan-4-ol (XIII).—A solution of 4.6 g. of XII in 150 cc. of water containing 2 cc. (a slight excess) of concentrated hydrochloric acid was shaken with 0.2 g. of palladous oxide under an atmosphere of hydrogen at room temperature until the theoretical amount of hydrogen had been absorbed. After removal of the catalyst by filtration, water was evaporated under reduced pressure. To the remainder was added 2 cc. of 50% of potassium carbonate solution, followed by further addition of solid potassium carbonate. This mixture was well agitated to remove water. Ether was then added, agitated well and decanted. This procedure was repeated several times. Ethereal portions were collected and, after drying over potassium carbonate, ether was removed on a water bath to leave a residue. Vacuum distillation of the residue gave 1.45 g. (56.2%) of a quite hygroscopic colorless viscous oil, b. p. 82°C/0.5 mm.

Anal. Found: C, 62.13; H, 11.80; N, 11.64. Calcd. for $C_6H_{13}ON$: C, 62.57; H, 11.38; N, 12.16%.

Picrolonate:—A mixture of 0.1 g. of XIII and 1 g. of picrolonic acid in 40 cc. of ethanol was heated on a water bath for a few min. and allowed to cool. The crystals were recrystallized from ethanol to brownish yellow prisms of m. p. 225°C (decomp.), 0.26 g.

Anal. Found: N, 18.33. Calcd. for $C_6H_{13}ON \cdot C_{10}H_8O_5N_4$: N, 18.46%.

1-Benzyl-4-chloro-1-azacycloheptane (XIV).—To a solution of 5.3 g. of XII in 50 cc. of dry benzene, was added dropwise under cooling in an ice-water bath a solution of 4 cc. of thionyl chloride in 5 cc. of dry benzene with stirring. The solvent was removed under reduced pressure, leaving a dark red residue. The residue was dissolved in a little water and

made alkaline with solid potassium carbonate. The oily substance was taken up in benzene and dried over potassium carbonate. After removal of benzene, vacuum distillation yielded 3.9 g. (67.3%) of a highly hygroscopic colorless liquid, b. p. 104~5°C/0.3 mm. which, on standing, gradually crystallized and showed the presence of halogen by Beilstein test.

Anal. Found: N, 6.10. Calcd. for $C_{13}H_{18}NCl$: N, 6.26%.

4-Amino-1-benzyl-1-azacycloheptane (XV) and bis-(4-benzyl-4-azacycloheptyl)-amine (XVI).—A mixture of 3.4 g. of XIV and 20 cc. of absolute ethanol saturated with ammonia at 0°C was heated in a sealed tube at 100°C for 3 hr. After cooling, the solvent was removed under reduced pressure, and the residue was dissolved in a little water and made alkaline with solid potassium carbonate. The liberated oil was extracted with benzene and dried over potassium carbonate. After removal of benzene, the residue was vacuum-distilled to yield 2.2 g. (71%) of a hygroscopic colorless oil (XV) of b. p. 105~6°C/0.4 mm. and 0.6 g. of a light yellow viscous oil (XVI) of b. p. 219~221°C/0.3 mm.

Anal. Found: N, 13.56. Calcd. for $C_{13}H_{20}N_2$ (XV): N, 13.71%. Found: C, 79.71; H, 9.46; N, 10.46. Calcd for $C_{26}H_{37}N_3$ (XVI): C, 79.74; H, 9.52; N, 10.73%.

XV on mixing with chloroauric acid produced a chloroaurate, which was recrystallized from water to give yellow micro plates, m. p. 194°C (decomp.).

Anal. Found: N, 3.13. Calcd. for $C_{13}H_{20}N_2 \cdot (HAuCl_4)_2$: N, 3.17%.

XVI gave a picrolonate by adding an ethanolic solution of picrolonic acid, which was recrystallized from a large amount of water to give yellow crystals, m. p. 213°C (decomp.).

Anal. Found: N, 16.45. Calcd. for $C_{26}H_{37}N_3 \cdot (C_{10}H_8O_5N_4)_2$: N, 16.75%.

4-Amino-1-azacycloheptane (XVII).—A solution of 2 g. of XV in 80 cc. of water was shaken with hydrogen in the presence of 0.2 g. of palladous oxide at room temperature until the theoretical amount of hydrogen had been absorbed. The catalyst was filtered off, and water was evaporated under reduced pressure. Vacuum distillation of the residue gave 0.55 g. (50%) of a highly hygroscopic colorless oil, b. p. 79~80°C/10 mm. When the distillate is allowed to stand in the atmosphere, white crystalline precipitates appeared in the oil under fuming, possibly because of absorption of carbon dioxide in the atmosphere. So the nitrogen content could not be determined.

On mixing with chloroauric acid, XVII gave a chloroaurate, which was recrystallized from water to yield yellow prisms, m. p. 209°C (decomp.).

Anal. Found: C, 9.18; H, 2.46; N, 3.47; Au, 48.9. Calcd. for $C_6H_{14}O_2 \cdot (HAuCl_4)_2$: C, 9.08; H, 2.03; N, 3.53; Au, 49.63%.

XVII and a saturated ethanolic solution of picric acid formed a picrate, which was recrystallized from ethanol to yield yellow prisms, m. p. 224°C (decomp.).

Anal. Found: N, 19.35. Calcd. for $C_6H_{14}N_2 \cdot (C_6H_3O_7N_3)_2$: N, 19.57%.

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The Centrifugal Distortion and the l-Type Doubling Constants in Linear XYZ-Type Molecules. The Determination of Force Field by These Constants

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I

It is usually impossible to determine the set of force constants for a molecule only through vibrational frequencies, unless isotopic substitution is made. Assumptions have frequently been made to reduce the number of unknown constants; one may mention examples of central force field, valence force field[1] or Urey-Bradley field[2]. It is, however, possible to use other experimental data than vibrational frequencies for obtaining the force constants. Wilson and Kivelson[3,4] showed that the centrifugal distortion constants of asymmetric top molecules can be used for the determination of the force constants in general force field. However, their results on sulfur dioxide[4] showed a discrepancy with those of infrared absorption spectra[5] based upon the isotopic substitution. An experimental error or other sources might contribute to this discrepancy, so that it is worth while to discuss about these points in a simpler system such as linear XYZ-type molecules.

The linear XYZ-type molecule has three fundamental modes: two of them are stretching vibrations along the molecular axis (parallel vibrations) and the other is a degenerate bending mode (perpendicular one). The force constant for the latter vibration can be determined by the value of frequency alone, but two observed frequencies are insufficient to determine three force constants associated with the former two modes. The centrifugal distortion constant will give additional information about the parallel vibrations. One may, however, note that there is another constant available: the *l*-type doubling constant. The Coriolis force lifts the degeneracy of the bending vibration and the separation between the two resulting energy states can accurately be measured by the microwave spectroscopy[6]. Since the centrifugal distortion and the *l*-type doubling constants give independent information, one can test the experimental error or the validity of the underlying assumption made in the theory. A sum rule is found to be useful for such a test.

II

The centrifugal force reduces the effective rotational constant and hence the rotational energy. The quantum mechanical expression for the energy decrease by centrifugal distortion is given by

$$\mathbf{H}_D=(1/2)(\mu_{xx}\mathbf{P}^2_x+\mu_{yy}\mathbf{P}^2_y) -(1/2)(\mu^e_{xx}\mathbf{P}^2_x+\mu^e_{yy}\mathbf{P}^2_y) \quad (1)$$

where $\mathbf{P}_x$ and $\mathbf{P}_y$ denote angular momentum operators, μ_{xx} and μ_{yy} inverses of moment of inertia, and the superscript e of μ refers to the equilibrium. Now μ_{xx} and μ_{yy} can be expanded as power series of the internal coordinates, ΔR_{XY} and ΔR_{YZ}, but the moment of inertia is usually defined in terms of Cartesian coordinates of individual atoms. The Cartesian coordinates of composing atoms are bound to each other by the complicated Eckart condition, and it is somewhat difficult to obtain the expansion of the moment of inertia in terms of internal coordinates. Hence it is very desirable to derive in general a relation between the normal coordinates and the Cartesian coordinates. The process using the **B**-matrix has already been discussed by the authors.[7] The relation is given by

1) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., New York, 1949.
2) H. C. Urey and C. A. Bradley, *Phys. Rev.* **38**, 1969 (1931).
3) D. Kivelson and E. B. Wilson, Jr., *J. Chem. Phys.* **20** 1575 (1952); **21**, 1229 (1953).
4) D. Kivelson, ibid. **22**, 904 (1954); L. Pierce, ibid. **24**, 139 (1956).
5) S. Polo and M. K. Wilson, ibid. **22**, 900 (1954).
6) R. G. Shulman and C. H. Townes, *Phys. Rev.* **77**, 421 (1950).
7) Y. Morino and E. Hirota, *J. Chem. Phys.* **23**, 737 (1955).

$$\mathbf{X}=\mathbf{M}^{-1}\mathbf{B}'\mathbf{U}'(\mathfrak{L}^{-1})'\mathbf{Q} \quad (2a)$$

$$=\mathbf{M}^{-1}\mathbf{B}'(\mathbf{L}^{-1})'\mathbf{Q} \quad (2b)$$

where $\mathbf{X}$ and $\mathbf{Q}$ denote the Cartesian coordinates and the normal coordinates matrices. $\mathbf{L}^{-1}$ is easily replaced by $\mathbf{L}$ through the relation $\mathbf{LL}'=\mathbf{G}$, or $\mathbf{L}^{-1}=\mathbf{L}'\mathbf{G}^{-1}$. [Cf. Eq. 20]

$$\begin{pmatrix}\Delta z_X\\ \Delta z_Y\\ \Delta z_Z\end{pmatrix}=\begin{pmatrix}\dfrac{(m_Y+m_Z)L_{11}+m_ZL_{31}}{m_X+m_Y+m_Z} & \dfrac{(m_Y+m_Z)L_{13}+m_ZL_{33}}{m_X+m_Y+m_Z}\\ \dfrac{-m_XL_{11}+m_ZL_{31}}{m_X+m_Y+m_Z} & \dfrac{-m_XL_{13}+m_ZL_{33}}{m_X+m_Y+m_Z}\\ \dfrac{-m_XL_{11}-(m_X+m_Y)L_{31}}{m_X+m_Y+m_Z} & \dfrac{-m_XL_{13}-(m_X+m_Y)L_{33}}{m_X+m_Y+m_Z}\end{pmatrix}\begin{pmatrix}Q_1\\ Q_3\end{pmatrix} \quad (4)$$

The expression of the $\mathbf{B}$-matrix is particularly simple in the present case; then it sufficices to consider only the Cartesian coordinates along the molecular axis (z-axis):

$$\mathbf{B}=\begin{pmatrix}1 & -1 & 0\\ 0 & 1 & -1\end{pmatrix} \quad (3)$$

Hence Eq. 2b becomes

The moment of inertia I_{xx} is given by

$$I_{xx}=\sum_i m_i(y_i^2+z_i^2)\cong\sum_i m_i z^e{}_i^2+2\sum_i m_i z^e{}_i\Delta z_i \quad (5)$$

where $y_i=\Delta y_i$ and $z_i=z^e{}_i+\Delta z_i$. The same expression holds for I_{yy}. Thus the inverse of the moment of inertia $\mu_{xx}=1/I_{xx}$ becomes

$$\mu_{xx}=(1/I^e{}_{xx})(1-2\sum_i m_i z^e{}_i\Delta z_i/I^e{}_{xx}+\cdots\cdots), \quad (6)$$

where the equilibrium positions of individual atoms $z^e{}_i$ can readily be calculated

$$z^e{}_X=[(m_Y+m_Z)R_{XY}+m_ZR_{YZ}]/(m_X+m_Y+m_Z), \quad (7a)$$

$$z^e{}_Y=[-m_XR_{XY}+m_ZR_{YZ}]/(m_X+m_Y+m_Z), \quad (7b)$$

and

$$z^e{}_Z=[-m_XR_{XY}-(m_X+m_Y)R_{YZ}]/(m_X+m_Y+m_Z). \quad (7c)$$

If one uses the relations Eqs. 4 and 7 in Eq. 6 the expansion of the inverse of the moment of inertia in normal coordinates is obtained :*

$$\mu_{xx}=\mu_{yy}=(1/I^e{}_{xx})(1-2(bQ_1+aQ_3)/(I^e{}_{xx})^{1/2}+\cdots). \quad (8)$$

a and b are constants including the force constants and given by

$$a=\frac{m_X(m_Y+m_Z)R_{XY}+m_Xm_ZR_{YZ}}{(m_X+m_Y+m_Z)(I^e{}_{xx})^{1/2}}L_{13}+\frac{m_Xm_ZR_{XY}+(m_X+m_Y)m_ZR_{YZ}}{(m_X+m_Y+m_Z)(I^e{}_{xx})^{1/2}}L_{33}, \quad (9a)$$

and

$$b=\frac{m_X(m_Y+m_Z)R_{XY}+m_Xm_ZR_{YZ}}{(m_X+m_Y+m_Z)(I^e{}_{xx})^{1/2}}L_{11}+\frac{m_Xm_ZR_{XY}+(m_X+m_Y)m_ZR_{YZ}}{(m_X+m_Y+m_Z)(I^e{}_{xx})^{1/2}}L_{31}, \quad (9b)$$

and between them there exists a useful relation noted by Nielsen :[8]

$$a^2+b^2=1 \quad (10)$$

When Eq. 8 is inserted into Eq. 1 and terms of the order of $Q^2{}_i$ are neglected,

$$\mathbf{H}_D=-\frac{bQ_1+aQ_3}{(I^e{}_{xx})^{3/2}}(\mathbf{P}^2{}_x+\mathbf{P}^2{}_y). \quad (11)$$

when the average of this term is taken over the vibrational state $(v_1, v^l{}_2, v_3)$, the first order energy $(v_1v^l{}_2v_3|\mathbf{H}_D|v_1v^l{}_2v_3)$ is equal to zero, but the second order perturbation gives

$$E_D=\frac{|(v_1v^l{}_2v_3|\mathbf{H}_D|v_1\pm1v^l{}_2v_3)|^2}{\mp h\nu_1}+\frac{|(v_1v^l{}_2v_3|\mathbf{H}_D|v_1v^l{}_2v_3\pm1)|^2}{\mp h\nu_3}=-4B^3{}_e\left[\frac{b^2}{(h\nu_1)^2}+\frac{a^2}{(h\nu_3)^2}\right][J(J+1)-1]^2. \quad (12)$$

Here $B_e=\hbar^2/2I^e{}_{xx}$ is the equilibrium rotational constant, and ν_1 and ν_3 are vibrational frequencies. Thus the centrifugal distortion constant D_e is given by

$$D_e=4B^3{}_e\left[\frac{b^2}{(h\nu_1)^2}+\frac{a^2}{(h\nu_3)^2}\right]. \quad (13)$$

The l-type doubling originates from the fact that the Coriolis interaction lifts the degeneracy of the bending vibration. This effect corresponds to an operator :[9]

$$\mathbf{H}_C=-\mathbf{h}_x\mathbf{P}_x-\mathbf{h}_y\mathbf{P}_y, \quad (14)$$

where

* μ_{xy} is equal to zero. It is to be noted that μ_{xx} and μ_{yy} are independent of the bending coordinates, Q_{2x} and Q_{2y}. (Cf. ref. 9)

8) H. H. Nielsen, *Revs. Modern Phys.* **23**, 90 (1951).
9) E. B. Wilson, Jr., and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).

$$\mathbf{h}_x=\frac{1}{2}[2\mu_{xx}\mathbf{p}_x+(\mathbf{p}_x\mu_{xx})+\mu_{xx}\mu^{1/2}(\mathbf{p}_x\mu^{-1/2})] \tag{15a}$$

and

$$\mathbf{h}_y=\frac{1}{2}[2\mu_{yy}\mathbf{p}_y+(\mathbf{p}_y\mu_{yy})+\mu_{yy}\mu^{1/2}(\mathbf{p}_y\mu^{-1/2})]. \tag{15b}$$

$\mathbf{p}_x$ and $\mathbf{p}_y$, vibrational angular momenta, are

$$\mathbf{p}_x=aQ_{2y}\mathbf{p}_1+bQ_{2y}\mathbf{p}_3-(aQ_1+bQ_3)\mathbf{p}_{2y} \tag{16a}$$

and

$$\mathbf{p}_y=-aQ_{2x}\mathbf{p}_1-bQ_{2y}\mathbf{p}_3+(aQ_1+bQ_3)\mathbf{p}_{2x}, \tag{16b}$$

respectively. The determinant of (μ_{xx}), μ, is simply μ^2_{xx}, because, $\mu_{xz}=\mu_{yz}$ and $\mu_{xy}=0$. Since direct calculation shows that the second and the third term of Eq. 15 cancel each other, Eq. 14 becomes

$$\begin{aligned}\mathbf{H}_C=&\frac{a}{I^e_{xx}}(Q_{2x}\mathbf{P}_y-Q_{2y}\mathbf{P}_x)\mathbf{p}_1\\&-\frac{a}{I^e_{xx}}(\mathbf{p}_{2x}\mathbf{P}_y-\mathbf{p}_{2y}\mathbf{P}_x)Q_1\\&+\frac{b}{I^e_{xx}}(Q_{2x}\mathbf{P}_y-Q_{2y}\mathbf{P}_x)\mathbf{p}_3\\&-\frac{b}{I^e_{xx}}(\mathbf{p}_{2x}\mathbf{P}_y-\mathbf{p}_{2y}\mathbf{P}_x)Q_3,\end{aligned} \tag{17}$$

where μ_{xx} is approximated by $(I^e_{xx})^{-1}$ [see Eq. 8]. For taking average of Eq. 17, it must be noted that Q_{2x} and Q_{2y} belong to a degenerate state, and hence the perturbation theory for a degenerate case should be applied. Here the first order perturbation energy also vanishes while the second order one is finite. When the two degenerate states are designated by $(v_1 1^{+1} v_3)$ and $(v_1 1^{-1} v_3)$,** according to their positive and negative angular momenta along the molecular axis, only an element $(v_1 1^{+1} v_3 | v_1 1^{-1} v_3)$ plays an essential role for the separation of these states: it is calculated as follows:

$$\begin{aligned}&\sum_{v'_1 v'_2 v'_3}\frac{(v_1 1^{+1} v_3|\mathbf{H}_C|v'_1 v''_2 v'_3)(v'_1 v''_2 v'_3|\mathbf{H}_C|v_1 1^{-1} v_3)}{E(v_1 1 v_3)-E(v'_1 v''_2 v'_3)}\\&=\frac{B^2_e}{h\nu_2}\left(1+4a^2\frac{\nu^2_2}{\nu^2_1-\nu^2_2}+4b^2\frac{\nu^2_2}{\nu^2_3-\nu^2_2}\right)J(J+1).\end{aligned} \tag{18}$$

Here $v'_1=v_1\pm1$, $v'_3=v_3\pm1$, and $v'_2=0^0$ and 2^0. Thus the l-type doubling constant q_e is given by

$$q_e=\frac{2B^2_e}{h\nu_2}\left(1+4a^2\frac{\nu^2_2}{\nu^2_1-\nu^2_2}+4b^2\frac{\nu^2_2}{\nu^2_3-\nu^2_2}\right). \tag{19}$$

Eqs. 13 and 19 for the centrifugal distortion and for the l-type doubling constant coincide with those given by Nielsen and others[8,10,11] though they are derived in slightly different manners.

III

Now the force constants to be obtained are implicitly included in the **L**-matrices and accordingly in the constants a^2 and b^2 defined by Eq. 9. On the other hand a^2 and b^2 are connected to each other by the sum rule, Eq. 10, and are given by the two observables, D_e and q_e, through Eqs. 13 and 19. Two of the three equations may be used for determining a^2 and b^2, and the other is available for testing possible errors in D_e and q_e or for confirming the approximation made in deriving Eqs. 13 and 19; that is the harmonic approximation. Table I gives the results of such calculations on several linear molecules of the XYZ-type. Some molecules, such as chlorine cyanide (ClCN) give reasonable values for a^2 and b^2, but others do not. One of the most definite inconsistency is the case of iodine cyanide; its D_e is probably in a considerable error.

D_e is really a correction term for the rotational energy and hence it cannot be obtained very accurately. On the other hand the measurement of q_e is easier, particularly in cases when the direct transition is possible to be observed as in hydrogen cyanide (HCN).[6]*** Since in Eq. 19 the second and the third term of q_e are useful in the calculation of the force constants and they are only about twenty percent of the total q_e, the error of q_e is exaggerated about six times in a^2 and b^2.

According to Eq. 9, b^2 (or a^2) thus determined gives a relation between L_{11} and L_{31} (or between L_{13} and L_{33}). In addition to this, another relation $\mathbf{LL}'=\mathbf{G}$, i.e.

$$\begin{aligned}&L^2_{11}+L^2_{13}=G_{11}=1/m_X+1/m_Y,\\&L^2_{31}+L^2_{33}=G_{33}=1/m_Y+1/m_Z,\\&L_{11}L_{31}+L_{13}L_{33}=G_{13}=G_{31}=-1/m_Y,\end{aligned} \tag{20}$$

determines the **L**-matrix, which gives the **F**-matrix by the relation $\mathbf{F}=(\mathbf{L}^{-1})'\mathbf{\Lambda}\mathbf{L}^{-1}$. Though the signs of the **L**-elements are not fixed in solving Eqs. 20, it does not

** Only $v_2=1$ state is interested here, so that $l=\pm1$.

10) G. Herzberg, *Revs. Modern Phys.* **14**, 219 (1942)

11) A. H. Nielsen, *J. Chem. Phys.* **11**, 160 (1943).

*** Recently direct l-type doubling transitions in ClCN were observed by L. Yarmus, (*Phys. Rev.* **105**, 928 (1957)).

TABLE I

a^2 AND b^2, AND EXPERIMENTAL DATA NECESSARY TO CALCULATE THEM.

Compound	$q+D$			q+sum rule		D+sum rule	
	b^2	a^2	a^2+b^2	b^2	a^2	b^2	a^2
HCN	0.9984	0.0501	1.0485	0.9218	0.0782	1.0305	−0.0305
^{35}ClCN	0.9246	0.0722	0.9968	0.9286	0.0714	0.9242	0.0758
^{79}BrCN	0.9511	0.0592	1.0103	0.9397	0.0603	0.9519	0.0481
^{127}ICN	1.2668	0.0301	1.2969	0.9613	0.0387	1.2816	−0.2816
OC^{32}S	0.9272	0.0460	0.9732	0.9576	0.0424	0.9217	0.0783
N_2O	1.0024	0.0398	1.0422	0.9436	0.0564	1.0235	−0.0235

Compound	(cm^{-1})[a]			B_0(Mc/s)	q(Mc/s)	D(Mc/s)
	$\tilde{\nu}^0_1$	$\tilde{\nu}^0_2$	$\tilde{\nu}^0_3$			
HCN	2089	712	3312	44315.97[c]	224.478[d]	0.09040[b]
^{35}ClCN	729	397	2201	5970.831[b]	7.459[b]	0.001663[b]
^{79}BrCN	580	368	2187	4120.221[b]	3.915[b]	0.0008844[b]
I^{127}CN	470	321	2158	3255.578[c]	2.69[c]	0.00088[c]
OC^{32}S	859	527	2079	6081.494[c]	6.39[c]	0.00127[c]
N_2O	1285	589	2224	12561.639[b]	23.736[b]	0.005359[b]

a) G. Herzberg, "Molecular Spectra and Molecular Structure", p. 174.
b) C. A. Burrus and W. Gordy, *Phys. Rev.* **101**, 599 (1956).
c) W. Gordy, W. V. Smith, and R. Trambarulo, "Microwave Spectroscopy", Table A4.
d) A. Miyahara, H. Hirakawa, and K. Shimoda, *J. Phys. Soc. Japan*, **11**, 335 (1956).
Values of b^2 with underline are used to calculate force constants.

TABLE II

FORCE CONSTANTS. (10^5 dynes/cm)

Compound	b^2	Present result			Herzberg[a]		Isotopic method[b]		
		F_{XY}	F_{YZ}	F'	F_{XY}	F_{YZ}	F_{XY}	F_{YZ}	F'
HCN	0.9218	5.90	16.93	0.36	5.8	17.9	6.257	18·68	−0.1907
^{35}ClCN	0.9246	4.74	18.35	1.31	5.2	16.7	4.7∼5.0	16.8∼18.2	0∼1
^{79}BrCN	0.9511	3.96	16.00	0.92	4.2	16.9			
OC^{32}S	0.9272	17.84	6.60	2.34	14.2	8.0			
N_2O	0.9436	18.34	11.06	1.63	13.7	14.6	17.88	11.39	1.36

a) G. Herzberg, "Molecular Spectra and Molecular Structure", p. 174
b) H. C. Allen, Jr., E. D. Tidwell and E. K. Plyler, *J. Chem. Phys.* **25**, 302 (1956) (HCN); W. S. Richardson and E. B. Wilson, Jr., ibid. **18**, 155, 694 (1950). (ClCN, N_2O).

influence the resulting F-matrix, and other solutions than those in Table II are not physically reasonable and can readily be rejected.

It must be noted that in the calculation described above $\tilde{\nu}^0_i$ and B_0 are respectively used instead of the quantities $\tilde{\nu}^e_i$ and B_e which should be used in the rigorous sense.

IV

In Table II the values of the force constants thus determined are compared with those from other sources, so far as available. The constants cited in Herzberg's book[1] are of central field type, the cross term being ignored. The diagonal terms show a little difference from the present ones. Richardson and Wilson[12] used isotopic molecules, $^{35}Cl^{13}CN$ and $^{15}N^{14}NO$, to obtain the three force force constants for chlorine cyanide and nitrous oxide. As was stated by them, the cross term F' plays an important role for nitrous oxide molecule: if one uses only two constants, F_{XY} and F_{YZ} to explain the observed $\tilde{\nu}^0_1$ and $\tilde{\nu}^0_3$ (rather than the zeroth order $\tilde{\nu}^e_1$ and $\tilde{\nu}^e_3$), then imaginary constants are resulted. They arrived at well-defined sets of force constants: $F_{XY}=17.88\pm0.7$, $F_{YZ}=11.39\pm0.3$, and $F'=1.36\pm0.3$, which are in close agreement with the values obtained above: $F_{XY}=18.34$, $F_{YZ}=11.06$, and $F'=1.63$. The substitution of ^{13}C for ^{12}C was found to be rather ineffective for determining the force constants of chlorine cyanide, so that only allowed ranges were reported for the three constants: $F_{XY}=4.7$ ∼5.0, $F_{YZ}=16.8$∼18.2, and $F'=0$∼1, which

12) W. S. Richardson and E. B. Wilson, Jr., *J. Chem. Phys.* **18**, 155, 694 (1950).

are favorably compared with ours: $F_{XY}=4.74$, $F_{YZ}=18.35$, and $F'=1.31$.

For hydrogen cyanide molecules, a rather complete analysis of vibration-rotation interaction was carried out together with that of DCN,[13,14] so that much more accurate values of force constants are available. As the *l*-type splitting is large for this molecule, it is possible to measure by the microwave spectroscopy[15] a direct transition between these doublets. With these data much more reliable values are expected in this molecule than in chlorine cyanide and nitrous oxide. However, the comparison made in Table II shows that the agreement for hydrogen cyanide is not better than those for chlorine cyanide and nitrous oxide. One of the reasons for this discrepancy may be considered to be the use of $\tilde{\nu}^0_i$ rather than $\tilde{\nu}^e_i$ in obtaining b^2. In fact, if $\tilde{\nu}^e_i$ is used ($\tilde{\nu}^e_1=2127.63\,\mathrm{cm}^{-1}$, $\tilde{\nu}^e_3=3442.81\,\mathrm{cm}^{-1}$ for hydrogen cyanide and $\tilde{\nu}^e_1=1953.18\,\mathrm{cm}^{-1}$, $\tilde{\nu}^e_3=2702.94\,\mathrm{cm}^{-1}$ for DCN)[14], b^2 changes to 0.8368 (q_e is used), but $F_{XY}=6.65$, $F_{YZ}=18.22$, and $F'=2.25$, thus the agreement of F' becomes worse.

If conversely the *l*-type doubling constant and the centrifugal distortion constant are calculated by using the force constants given in reference 14, they are 215.68 Mc and 0.08406 Mc, respectively, which are compared with the observed, 224.478 Mc[15] and 0.9040 Mc.[16] These differences (8.80 Mc or 3.9% for the *l*-type doubling constant and 0.00634 Mc or 7.0% for the centrifugal distortion constant) are definitely larger than the errors involved in the observed values. The higher order effects such as anharmonicity of vibrations or higher terms in the expansion of μ_{zz} can produce this order of discrepancy for the two constants. According to the measurement of Douglas and Sharma[13] α/B is about 0.007 and $\omega_e x_e/\omega_e$ about 0.015. Exact expression for the higher order effect has been given only for the centrifugal distortion constant of diatomic molecule, but for polyatomic molecules it would be too complicated to be calculated exactly. One way to avoid the difficulty is to use in Eqs. 13 and 19 B_0 instead of B_e and $\tilde{\nu}^0_i$ for $\tilde{\nu}^e_i$: the *l*-type doubling constant of hydrogen cyanide increases to 221.45 Mc and the centrifugal distortion constant to 0.08722 Mc, though an exact agreement is not obtained.

For molecules including no hydrogen atom these higher order effects are not very critical, α/B and $\omega_e x_e/\omega_e$ being smaller (e.g. α/B of chlorine cyanide is 0.0027). Fairly good coincidence obtained for cases of chlorine cyanide and nitrous oxide can, therefore, be understood.

13) A. E. Douglas and D. Sharma, ibid. **21**, 448 (1953).
14) H. C. Allen, Jr., E. D. Tidwell and E. K. Plyler, ibid. **25**, 302 (1956).
15) See, for example, A. Miyahara, H. Hirakawa and K. Shimoda, *J. Phys. Soc. Japan*, **11**, 335 (1956).
16) C. A. Burrus and W. Gordy, *Phys. Rev.* **101**, 599 (1956).

Note added in proof.

Recently Wilson gave an expression for the centrifugal distortion constant of linear molecules. [E. Bright Wilson, Jr., *J. Chem. Phys.* **27**, 986 (1957)] The result obtained in the present paper [Eq. 13] can be shown to be in complete agreement with his formula, by some minor transformations.

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Isolation of Agarobiose Derivative from the Mucilage of Gloiopeltis Furcata

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The mucilage of a red seaweed *Gloiopeltis furcata** resembles carrageenin (the mucilage of *Chondrus* algae) in the respect that it has a high content of sulfate residues as well as that it forms on dissolution in water a highly viscous solution. But our recent report has pointed out the chemical difference that the *Gloiopeltis* mucilage is chiefly composed of D-galactose and 3,6-anhydro-L-galactose as in the case of agar[1], while that carrageenin is composed of D-galactose and the anhydro-D-sugar, an enantiomorph of the above one[2]. Thus the complete methanolysis of the former mucilage afforded methyl D-galactoside and 3,6-anhydro-L-galactose dimethylacetal together with a small amount of a L-galactose derivative[1]. On the other hand, partial methanolysis of agar led to the isolation of crystalline agarobiose dimethylacetal (4-*O*-β-D-galactopyranosyl-3,6-anhydro-L-galactose dimethylacetal) in a good yield[3] and also of crystalline 4-*O*-(4,6-*O*-1′-carboxyethylidene-β-D-galactopyranosyl)-3,6-anhydro-L-galactose dimethylacetal as an acidic product in a slight yield[4]. With this in mind, the *Gloiopeltis* mucilage has been subjected to partial methanolysis, the results being reported herein.

The partial methanolysis has been conducted by refluxing the suspension of the mucilage in 0.5% methanolic hydrogen chloride for two hours as in the case of agar[3]. The methanolysate was treated with a barium hydroxide solution to effect saponification and then with cation- and anion-exchange resin in succession. An acidic substance, which was adsorbed by the anion-exchange resin, was eluted therefrom by displacement with excess of sulfuric acid and isolated as a barium salt. The salt has proved to be entirely barium methylsulfate, derived from sulfate residues present in the mucilage molecule. No evidence was obtained to indicate the presence of pyruvic acid[5] or any other carboxylic acid.

The neutral methanolysate, which passed through the resins without being retained, was subjected to charcoal chromatography[6], which led to the isolation of methyl D-galactoside (6%), a mixture of 3,6-anhydro-L-galactose dimethylacetal (4%) and methyl D-xyloside (2%), and agarobiose dimethylacetal (55%), the yields being based on the neutral methanolysate by weight.

The mixture of 3,6-anhydro-L-galactose dimethylacetal and methyl D-xyloside was further resolved into the components by chromatography on a powdered filter paper column. The methyl D-xyloside, obtained as a syrup, was hydrolyzed to give the free sugar, which was then identified as crystalline di-*O*-benzylidene-D-xylose dimethylacetal after Breddy and Jones[7]. This has been the first report as to the identification of D-xylose as far as the *Gloiopeltis* mucilage is concerned. But the yield was so low that the sugar might be possibly derived from a contaminating xylan.

Agarobiose dimethylacetal has been isolated as crystals, the physical constants of which are identical with those of the sample isolated previously from agar by two of the present writers[3]. The dimethylacetal was hydrolyzed and subsequently converted into agarobiose phenylosazone, which again agreed well with an authentic sample. On acetylation the dimethylacetal yielded hexa-acetate melting at 136~137°C, the value being in disagreement with the melting point 87~88°C reported previously by two of the writers[3], but in agreement with the melting point 137.5~138.5°C reported recently by Clingman, Nunn and Stephen[8]. The experiment

* Japanese name is "Fukuro-funori".

1) S. Hirase, C. Araki and T. Itô, This Bulletin, **29**, 985 (1956).
2) C. Araki and S. Hirase, ibid., **29**, 770 (1956); A. N. O'Neill, *J. Am. Chem. Soc.*, **77**, 2837, 6324 (1955).
3) C. Araki and S. Hirase, This Bulletin, **27**, 109 (1954).
4) S. Hirase, ibid., **30**, 70, 75 (1957).
5) S. Hirase, ibid., **30**, 68 (1957).
6) R. L. Whistler and D. F. Durso, *J. Am. Chem. Soc.*, **72**, 677 (1950).
7) L. J. Breddy and J. K. N. Jones, *J. Chem. Soc.*, **1945**, 738.
8) A. L. Clingman, J. R. Nunn and A. M. Stephen, ibid., **1957**, 197.

was repeated, but the acetate melting at 87~88°C could be prepared neither from the dimethylacetal of a *Gloiopeltis* origin nor from that of an agar origin.

It necessarily follows from the isolation of the agarobiose derivative that D-galactopyranose residues are connected through β-galactoside links with the 4-positions of 3,6-anhydro-L-galactose residues to form agarobiose residues in the mucilage molecule, and that if sulfate residues are left out of consideration, the disaccharide represents the repeating unit in the molecule of the mucilage as in that of agarose, a principal polysaccharide of agar[9].

Experimental

Evaporation and concentration of solutions were carried out under reduced pressure below 40°C. The melting points are uncorrected.

Partial Methanolysis of the Mucilage. — The mucilage preparation used in this study was the same one as that used in the previous work[1]. The mucilage (10 g., moisture 9.33%), after being soaked in 0.5% methanolic hydrogen chloride (100 cc.) overnight at room temperature, was heated under reflux for two hours, and then undissolved material (1.8 g.) was filtered off, washed with methanol and dried in vacuo. The filtrate and washings were combined, neutralized with silver carbonate, refiltered and evaporated to a syrup (9.0 g.). It was then heated with 0.3 N barium hydroxide solution (80 cc.) at 60°C for two hours to effect saponification, excess of the barium hydroxide removed by neutralization with carbon dioxide and subsequent filtration, and the filtrate was concentrated to a syrup, which was dried by repeated dissolution in methanol followed by evaporation; yield 7.3 g.; $[\alpha]_D^{13}$ −9.6° (*c* 0.83 in water).

Barium Methylsulfate.—The syrup obtained above was dissolved in water, the resulting solution allowed to pass through columns of the cation-exchange resin Amberlite IR-120 (100 cc) and the anion-exchange resin Amberlite IR-4B (100 cc.) in succession, and the columns were washed with water (1.3 *l.*). The combined effluents and washings were evaporated to recover the neutral methanolysate, which formed a syrup; yield 4.3 g. (59% of the consumed mucilage on the moisture-free basis); $[\alpha]_D^{13}$ −10.7° (*c* 0.75 in water).

The IR-4B resin, which adsorbed an acidic substance, was transferred to a beaker and stirred with 2 N sulfuric acid (100 cc.) under ice-cooling for a brief period of time. The resin was retransferred to a glass tube to form a column, excess of the liquid allowed to drain, and the column was washed with additional 100 cc. of 2 N sulfuric acid and water in succession. All the effluents were combined, neutralized immediately with a hot saturated barium hydroxide solution, filtered and evaporated, the residue being obtained as a colorless solid; yield 3.5 g.; $[\alpha]_D^{13}$ ±0° (*c* 1.0 in water). Paper chromatographic examination showed the absence of any carbohydrate compound. Determination of the ash content proved that the solid obtained above was barium methylsulfate;

Anal. Found: Ash (as barium sulfate), 83.2. Calcd. for $(CH_3SO_4)_2Ba \cdot H_2O$: $BaSO_4$, 83.3%.

Chromatography of the Neutral Methanolysate. — The neutral methanolysate (4.3 g.), obtained above from the effluent which passed through the ion exchangers, was dissolved in water (100 cc.), and the solution was soaked into the top of a charcoal*-Celite column (5.0×20 cm.), which was then developed successively with water, 2%, 5%, 7.5%, 15% and 30% ethanol in water. The effluents were separately evaporated to dryness, and the resultant residues were weighed, measured for specific rotation, and examined on paper chromatograms[6], which were irrigated with *n*-butanol-ethanol-water (4 : 1 : 2 v/v) and which were sprayed with *o*-aminophenol reagent[10]. The results are given in Table I.

Experiments described below enabled the following identification: fraction I as methyl D-galactoside, fraction II as a mixture of 3,6-anhydro-L-galactose dimethylacetal and methyl D-xyloside, and fraction IV as agarobiose dimethylacetal. From the paper chromatographic examination, there was also obtained an indicative evidence to show that fraction III was a mixture of 3,6-anhydro-L-galactose dimethylacetal and agarobiose dimethylacetal, and that fractions V, VI and VII were mixtures of higher oligosaccharide derivatives. But these fractions were not studied.

Identification of Methyl D-Galactoside. — Fraction I was dissolved in 95% ethanol and the solution left in a refrigerator, when methyl D-galactoside was obtained as crude crystals of monohydrate; yield 0.06 g.; m. p. and mixed m. p. 95~98°; $[\alpha]_D^{12}$ +172° (*c* 0.57 in water); OCH_3, found 14.69% (calculated for $C_6H_{11}O_5(OCH_3) \cdot H_2O$: 14.62%).

The mother liquor was concentrated to a syrup (0.18 g.), which was then subjected to hydrolysis with 1N sulfuric acid in the usual manner, affording D-galactose; yield 0.15 g.; m. p. and mixed m. p. 160°C; $[\alpha]_D^{12}$ +81.3° (an equilibrium value, *c* 0.64 in water).

Separation and Identification of 3,6-Anhydro-L-galactose Dimethylacetal and Methyl D-Xyloside. — Fraction II showed two distinct spots on a paper chromatogram; one was yellowish brown in color, corresponding to 3,6-anhydro-L-galactose dimethylacetal, and the other blue in color, corresponding to methyl D-xyloside. The mixture (0.38 g.) was separated on a column of powdered filter paper, *n*-butanol-water (6 : 1 v/v)

9) C. Araki, This Bulletin, **29**, 543 (1956); *Mem. Fac. Ind. Arts, Kyoto Tech. Univ.*, **5**, 21 (1956).

10) S. Hirase, C. Araki and S. Nakanishi, This Bulletin, **26**, 183 (1953).

* Charcoal used was "Shirasagi", manufactured by Takeda Pharmaceutical Industries, Ltd., Osaka.

TABLE I

CHROMATOGRAPHIC SEPARATION OF THE NEUTRAL METHANOLYSATE

Fraction	I	II	III	IV	V	VI	VII
Developer	W	2% E	5% E	5% E	7.5% E	15% E	30% E
〃 (*l.*)	3.0	3.6	0.7	9.3	3.0	4.0	3.0
Yield (g.)	0.26	0.38	0.10	2.37	0.13	0.62	0.57
$[\alpha]_D$ (° in W)	+98	+17	−22	−27	−10	−4	−19

W: Water E: Ethanol

being used as a mobile phase. The effluents (7 cc. per fraction) were examined on paper chromatograms and the fractions showing the same contents were combined and evaporated to dryness, two main components being recovered as colorless syrups, respectively.

The faster-moving component was proved to be 3,6-anhydro-L-galactose dimethylacetal; yield 0.19 g.; $[\alpha]_D^{12}$ −26.0° (*c* 0.50 in water); OCH_3, found: 28.72% (calculated for $C_6H_{10}O_4(OCH_3)_2$: 29.81%). When hydrolyzed with 0.02 N sulfuric acid in a boiling water bath for two hours, it afforded 3,6-anhydro-L-galactose (0.12 g.) in a syrupy form. The sugar was identified by its conversion into the phenylosazone in the usual manner[11]; m. p. and mixed m. p. 217°C; $[\alpha]_D^{15}$ −52.0° (*c* 0.50 in pyridine-methanol (2 : 3)).

The slower moving component was proved to be methyl D-xyloside; yield 0.10 g.; $[\alpha]_D^{18}$ +28.0° (*c* 0.50 in water). On hydrolysis with N sulfuric acid in the usual manner, it afforded D-xylose in a sirupy form; yield 0.06 g.; $[\alpha]_D^{18}$ +18.8° (*c* 1.28 in water). The sugar was dissolved in one cc. of Breddy and Jones' reagent[7] which consisted of benzaldehyde (4 cc.) and 0.36 N methanolic hydrogen chloride (14 cc.), and the resulting solution was let stand for a week at room temperature. The di-*O*-benzylidene-D-xylose dimethylacetal which formed was filtered off, washed with water and methanol in succession, and dried at 100°C; yield 0.05 g.; m. p. 207～208°C. Recrystallization from chloroform-ligroin afforded needles; m. p. 208～209°C; $[\alpha]_D^{18}$ −10° (*c* 1.0 in chloroform). Admixture with an authentic sample showed no depression of the melting point.

Anal. Found: C, 66.98; H, 6.51. Calcd. for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50%.

Identification of Agarobiose Dimethylacetal.—Fraction IV of the charcoal chromatography was dissolved in ethanol (5 cc.), acetone (5 cc.) added, and the resulting solution was left in a refrigerator. Crystals of agarobiose dimethylacetal were filtered off, washed with ethanol and dried; yield 1.91 g.; m. p. 162～163°C. Recrystallization was best effected by dissolving the crude crystals in hot methanol, adding a double volumes of acetone, filtering the resulting solution while it was hot, and allowing the filtrate to cool. Pure agarobiose dimethylacetal formed colorless prisms; m. p. 165～166°C; $[\alpha]_D^{10}$ −29.3° (*c* 1.50 in water); $[\alpha]_D^{10}$ −38.7° (*c* 1.50 in methanol). Two of the writers report m. p. 162～164°C, $[\alpha]_D$ −29.1° (in water) and $[\alpha]_D$ −37.4° (in methanol)[3], and Clingman, Nunn and Stephen report m. p. 163～166°C and $[\alpha]_D$ −36° (in methanol)[8]. Admixture with an authentic sample showed no depression of the melting point.

Anal. Found: C, 45.20; H, 7.23; OCH_3, 16.74. Calcd. for $C_{12}H_{20}O_9(OCH_3)_2$: C, 45.40; H, 7.07; OCH_3, 16.76%.

Agarobiose Phenylosazone.—Agarobiose dimethylacetal obtained above was heated in 0.02 N sulfuric acid in a boiling water bath for two hours to effect hydrolysis, and the resulting agarobiose was converted into its phenylosazone in the usual manner. The crude osazone obtained was purified by recrystallization from ethanol, forming yellow crystals; m. p. 219～220°C; $[\alpha]_D^{10}$ −136.6° (an initial value, *c* 0.41 in pyridine-ethanol (2 : 3)) → −107.3° (after forty-eight hours). The values reported from this laboratory are m. p. 218～219°C[12], 220～221°C[13] and 221～222°C[13], and $[\alpha]_D$ −108.8°[3] and −110.8°[13] in pyridine-ethanol (2 : 3). Clingman and others report m. p. 222～223.5°C and $[\alpha]_D$ −115° in the same solvent mixture[8]. Admixture with an authentic sample showed no depression of the melting point.

Hexa-*O*-acetylagarobiose Dimethylacetal.—Agarobiose dimethylacetal (0.5 g.) obtained above was acethylated with acetic anhydride (5 cc.) and pyridine (5 cc.) for two days at room temperature. When the reaction solution was poured into a mixture of ice and water with stirring, the hexaacetate was precipitated as fine powders, which were then filtered off, washed with water and dried in vacuo; yield 0.7 g.; m. p. 136～137°C. The crude crystals were recrystallized from methanol-water (1 : 2), affording the pure acetate in stout needles; m. p. 136～137°C; $[\alpha]_D^{10}$ −5.8° (*c* 1.20 in chloroform) and $[\alpha]_D^{10}$ −12.5° (*c* 1.20 in benzene). Two of the writers reported m. p. 87～88°C, $[\alpha]_D$ −5.8° (in chloroform) and −12.5° (in benzene)[3], and Clingman and others report m. p. 137.5～138.5°C and $[\alpha]_D$ −13.5° (in benzene)[8].

Anal. Found: C, 50.11; H, 6.28; OCH_3, 9.66; $COCH_3$, 41.57. Calcd. for $C_{12}H_{14}O_9(COCH_3)_6(OCH_3)_2$: C, 50.16; H, 6.15; OCH_3, 9.97; $COCH_3$, 41.57%.

Since the observed melting point was in disagreement with that reported by two of the writers, acetylation was re-examined for agarobiose dimethylacetal isolated from agar, but the result was exactly the same as that described above. The reason for the discrepancy is obscure.

11) C. Araki, *J. Chem. Soc. Japan, (Nippon Kagaku Kaishi)*, **65**, 725 (1944).

12) C. Araki, ibid., **65**, 533 (1944).

13) S. Hirase and C. Araki, This Bulletin, **27**, 105 (1954).

Summary

1. The mucilage of *Gloiopeltis furcata* has been subjected to partial methanolysis, which resulted in the isolation of methyl D-galactoside, 3,6-anhydro-L-galactose dimethylacetal, methyl D-xyloside and agarobiose dimethylacetal.

2. Since the agarobiose derivative was obtained in a good yield, it has been concluded that the disaccharide represents the chief repeating unit of the mucilage molecule, if the sulfate residues present in the mucilage are left out of consideration.

3. Xylose has been identified for the first place so far as the *Gloiopeltis* mucilage is concerned. But the yield was so low that the sugar might be possibly derived from a contaminating xylan.

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The Determination and the Solubility of Water in Liquid Sulfur Dioxide

By Daisaburo MURAKAMI and Niichiro TOKURA

(Received December 27, 1957)

Liquid sulfur dioxide has been used in a large scale as a selective solvent for separation of aromatic hydrocarbons in petroleum or as bleaching, fumigating, antiseptic, or refrigerating agent. Recently it has been used as a non-aqueous solvent frequently in inorganic and organic synthetic reactions just like liquid ammonia. But it has a defect as a solvent owing to the presence of a small quantity of water. The corrosion of industrial equipments is largely due to minute amount of water contained in it. The amount was therefore defined to be below 50 p. p. m. by the Sulfur Dioxide Committee[1] in U. S. A. in 1933, the required accuracy for the analytical method being 1~2 p. p. m. .

It is also anticipated that the reaction process and the rate are largely affected by a minunte amount of water in sulfur dioxide in case of organic ionic reactions. The determination of water in sulfur dioxide was studied for the first time in 1931.[2,3] The method was consisted of a dehydration of water in liquid sulfur dioxide with phosphorus pentoxide. A titration method using the Karl Fischer (abridged as K. F.) reagent was proposed by Karl Fischer in 1935[4] and lately reformed by Dicaprio[5] to make the analysis of water in liquid sulfur dioxide easier. In the dehydration method[2,3] the liquid sulfur dioxide to be analyzed was evaporated, passed through a tube containing phosphorus pentoxide and the water absorbed in the tube was determined. In this method, it was pointed out by Zavarov[3] that an intolerable amount of water yet remained in the dioxide when more than 0.01% of water was contained in the original sample.

In the Dicaprios method[5], it is difficult to pick up the sample accurately, the manipulation is inconvenient as it required a low-and constant temperature room and the K. F. reagent changes in quality by the lapse of the storing time.

The writers have devised a simple and accurate measuring method of water in liquid sulfur dioxide, improving the method of the K. F. titration.

On application of the new method, the solubility curve of water in liquid

1) F. A. Eustass, *Ind. Eng. Chem., Anal. Ed.*, **5**, 77 (1933).
2) A. Scribner, *Ind. Eng. Chem., Anal. Ed.*, **3**, 255 (1931).
3) G. V. Zavarov, *Zavodskaya. Lab.*, **5**, 1314 (1936); J. Mitchell and D.M. Smith, "Aquametry", Interscience Publishers, Inc., New York. p. 236 (1948).
4) K. Fischer, *Angew. Chem.*, **48**, 394 (1935).
5) B. R. Dicaprio, *Anal. Chem.*, **19**, 1010 (1947).

sulfur dioxide at ordinarily adopted temperatures has been traced. Also a convenient method for drying liquid sulfur dioxide is discussed by estimating the residual water in the dried liquid sulfur dioxide by the present analytical procedure. Two points of improvement are involved in this method as shown in the following.

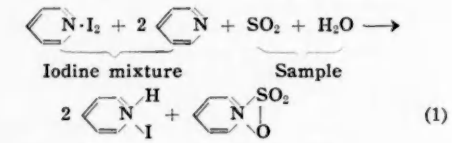
Firstly, as sulfur dioxide constitutes a component of the K. F. reagent, there is no need to use the so called K. F. reagent. It is satisfactory only to add a mixture of iodine and pyridine in methanol (abridged as iodine mixture) to the sample (liquid sulfur dioxide).

Secondly, to avoid the operative difficulties and the loss due to evaporation in sampling, weighing and titration it has been devised to take up the sample in a small glass pressure bottle to be weighed and put into a titration flask, chilled to about $-40°C$ by dry ice.

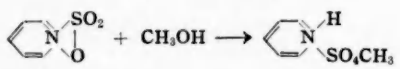
A K. F. reagent is prepared instantly and caused to react with the water in the sample at the same moment when a definite amount of the iodine mixture is added to the titration flask. The excess of the iodine mixture is back-titrated by an aqueous methanol, of a known water-equivalent value. The iodine mixture can be kept for a long time without change. Accuracy is also raised by the direct weighing of the sample in the pressure bottle before and after the charge into the flask.

As this method is very convenient in its manipulation, it may be used as a rapid routine analysis in factories. The accuracy of this method was found to be satisfactory. The differences between added water (5 to 30 mg.) in the sample and the water found by this procedure were zero to ± 0.06 mg.

In the titration flask, the following series of reaction is occurring and, even at $-40°C$, the K. F. reaction has been proved to proceed quantitatively[6].



$$2 \text{ (pyridine-HI)} + \text{(pyridine-SO}_2\text{)} \qquad (1)$$



$$+ \text{CH}_3\text{OH} \longrightarrow \text{(pyridine-H, SO}_4\text{CH}_3\text{)} \qquad (2)$$

6) G. Toennies and M. Elliott, *J. Am. Chem. Soc.*, **59**, 902 (1937).
7) K. Wickert, *Z. anorg. allgem. Chem.*, **239**, 89 (1938).

The solubility of water in liquid sulfur dioxide was measured by Wickert[7] only at 22°C and no other study at different temperatures has been reported. We have measured the solubility of water in liquid sulfur dioxide at various temperatures utilizing the above-mentioned method. (cf. Table I.)

TABLE I
SOLUBILITY OF WATER IN LIQUID SULFUR DIOXIDE

Temp. °C	Solubility g. H_2O/100 g. liq. SO_2
30	2.68
22	2.29
15	1.88
5	1.50
0	1.20
−10	0.81
−20	0.55
−30	0.37
−50	0.22

One part of liquid sulfur dioxide in equilibrium with water in a pressure bottle at a definite temperature was introduced into a small pressure bottle and the water in it was determined by the above described method. Thus the solubility of water in liquid sulfur dioxide in the range between $-50°C$ and $+30°C$ was measured. The solubility at 22°C (2.29 g. H_2O/100 g. liq. SO_2) was well conformed with the Wickert's result (2.3 g. H_2O/100 g. liq. SO_2)[7].

From the solubility value obtained as above, a linear plot of the logarithm of the solubility as a function of the reciprocal

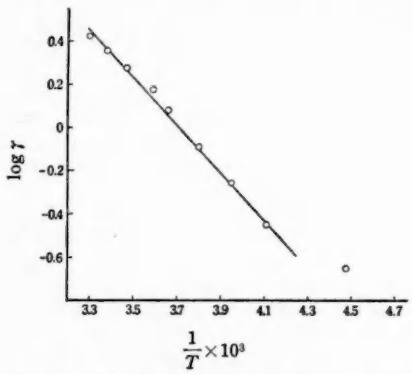


Fig. 1. Solubility of water in liquid sulfur dioxide as a function of temperature.
$\log \gamma = Q/RT + C$ (1), where, Q: heat of solution, γ: solubility, T: absolute temperature, R: gas constant and C: a constant.

of the absolute temperature is given in Fig. 1, using the following thermodynamic equation (1): the heat of solution of water in liquid sulfur dioxide is found to be 5.04 kcal./mole (endothermic) for the range between −50°C and +30°C (Table II.).

TABLE II

HEAT OF SOLUTION OF WATER IN LIQ. SO_2

C=4.095 in eq. (1)

Temp. °C	Heat of Soln. Q kcal./mole
30	5.08
22	5.05
15	5.03
5	4.99
0	5.01
−10	5.03
−20	5.04
−30	5.09

Mean Q=5.04 kcal./mole.

Method of the Measurement

(1) Reagents.—Pyridine was dehydrated with potassium hydroxide and distilled. Methanol was dried with metallic magnesium and distilled. Liquid sulfur dioxide was purified and dehydrated with concentrated sulfuric acid and distilled.

The iodine mixture was prepared by mixing the above three materials so that the molar ratio of iodine, pyridine and methanol was to be 1 : 10 : 40. It may be better to increase the quantity of methanol when the water content in the sample was very small. The methanol-water mixture to be used for the back titration was prepared by mixing 1 mole of water with 100 moles of methanol. The water-equivalent value of the iodine mixture and the content of water in aqueous methanol should be previously determined by a standard Karl Fischer's method[4].

(2) Titration apparatus and manipulation.—An ordinary K. F. titration apparatus with conductometrical titrating device was used except that the titrating flask was equipped with a inlet glass tube with a stop cock to connect a small cylindrical pressure bottle (10 cm. long and 2.5 cm. inner diameter) with a valve or cock on its top, containing the sample (Fig. 2).

The flask and the pressure bottle were connected tightly by a couple of jointing screw pieces made of stainless steel. Liquid sulfur dioxide was condensed into this small pressure bottle with cooling and closed. After weighing, the pressure bottle was connected to the titrating flask. Space in the flask was previously replaced with perfectly dried air. The flask was cooled to −40°C with dry ice and ethanol, and the cock of the flask and the valve of the pressure bottle were carefully opened to let the sample flow into the flask. Then the valve and the cock were closed. The pressure bottle was disconnected from the flask and the weight of the empty bottle was again examined. When necessary, the sample was diluted with some more liquid sulfur dioxide of a known water content.

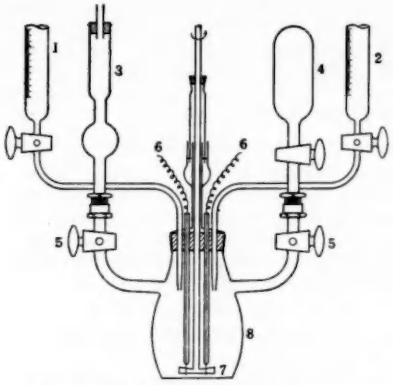


Fig. 2. Titration assembly.
1: Iodine mixture
2: Standard aqueous methanol
3: Drying tube
4: Glass pressure bottle
5: Stainless steel joint
6: Platinum electrode
7: Glass stirrer
8: Titrating flask

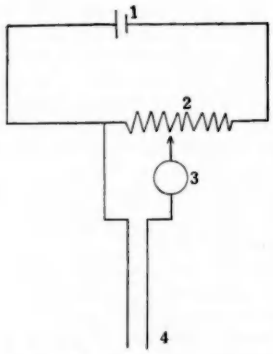


Fig. 3. Circuit diagram.
1: Battery
2: Rheostat
3: Galvanometer
4: Platinum wire electrode.

As the path between the cock of the flask and the valve or cock of the pressure bottle is very short and made of a thin capillary, the loss due to the wetting or the vaporization of sulfur dioxide is small. The sample was taken to make the water amount about 10 mg. After the sample had been taken up in the titration flask, known amount of iodine mixture was slowly introduced into the flask with stirring and cooling, and its excess was back-titrated with aqueous methanol. The end-point was indicated by applying the dead-stop method (initial E. M. F., 10 mV.) according

to Foulk and Bawden[8,9], a rheostat, a galvanometer, a cell and two platinum electrodes being arranged as shown in Fig. 3.

(3) Calculation.—Water content x (g. H_2O/g. liq. SO_2 or 10^{-6} p. p. m. of liq. SO_2) is calculated by the following equation:

$$x = (\alpha A - \beta B)/G,$$

Here A, amount of iodine mixture used (cc.); α, water-equivalent of the iodine mixture (g. H_2O/cc.); B, amount of the aqueous methanol consumed for the back titration (cc.); β, water content of the aqueous methanol (g. H_2O/cc.); G, weight of the sample (g.).

Results and Discussion

(1) Accuracy.—To examine the accuracy of the present method, a slight amount of water (5 to 30 mg.) dissolved in methanol was titrated. The result was satisfactory as described above. The difference between the added and the found was less than ± 0.06 mg.

(2) Solubility of water in liquid sulfur dioxide.—After equilibrium is reached by heeping a mixture of purified liquid sulfur dioxide and distilled water for four hours in a thermostat maintained at a given temperature, a part of the liquid sulfur dioxide (lower layer) was introduced into another small pressure vessel. The water was then determined by the present method. The equilibrium was obtained within three hours. The fluctuation in temperature was less than ± 0.05°C at above zero degree and ± 0.5°C below zero degree.

The results are shown in Table I, showing an increase in solublility as the temperature increases.

(3) Heat of solution of water in liquid sulfur dioxide.—A plot of $\log \gamma$ vs. T^{-1} (Fig. 1) was given as a straight line. The value of C in eq. 1 was determined as 4.095 from the plot. The heat of solution was calculated from equation 1 as 5.04 kcal./mole.

(4) Comparison of the efficiency of various dehydrating agents for liquid sulfur dioxide.—Liquid sulfur dioxide was dehydrated using a pressure bottle with various dehydrating agents. Namely, liquid sulfur dioxide (water content: 0.16g./100 g. SO_2) was tapped into pressure bottles filled with a definite amount of concentrated sulfuric acid, phosphorus pentoxide, active alumina, drierite and silica gel, respectively and was allowed to stand for 12 hours for dehydration.

Then the samples were taken up into measuring pressure-bottles and titrated by the present method, the results being as the following: (Table III).

TABLE III

MEASUREMENT OF WATER IN LIQUID SULFUR DIOXIDE DEHYDRATED WITH VARIOUS DRYING AGENTS

Desiccant	Added g.	Liq. SO_2 g.	H_2O p. p. m.
Sulfuric acid	30	180	110
Phosphorus pentoxide	30	180	48
Active alumina	30	180	80
Drierite	30	180	82
Silica gel	30	180	98

It was observed that phosphorus pentoxide had the most powerful dehydrating ability for liquid sulfur dioxide. In the former experiment[10], about one-meter tube filled with phosphorus pentoxide was used for the dehydration of liquid sulfur dioxide which can be replaced by phosphorus pentoxide in a pressure bottle for easier handling with satisfactory result.

A part of the expense used in the present study was defrayed by the Scientific Research Fund of the Ministry of Education. Liquid sulfur dioxde was donated by the Befu Chemical Industries Co., Ltd. Reagents used for this investigation were given by Mr. M. Nuiya, the Reagent Manufacturing Division of the Mitsubishi Chemical Industries Co., Ltd. together with encouraging suggestions. The authors wish to express their sincere thanks to these helps and donations.

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8) C. W. Foulk and A. T. Bawden, *J. Am. Chem. Soc.*, **48**, 2045 (1926).

9) G. Wernimont and F. J. Hopkinson, *Ind. Eng. Chem., Anal. Ed.*, **15**, 272 (1943).

10) K. Ziegler and H. Wollschitt, *Ann.*, **477**, 90 (1930).

Studies on the Proton Transfer in Organic Salts by the Dipole Moment Measurements

By Hiroshi TSUBOMURA

(Received December 21, 1957)

Kraus et al.[1] and Maryott[2] measured independently dipole moments of picrates of alkylamines in benzene and in dioxane solutions, and reported that the dipole moments measured lie between 12 and 13 *D*. As they recognized, these large dipole moments can be explained by assuming that the acid AH and the base B form an ion pair such as $A^-...H-B^+$.

Such a proton transfer from acid to base in non-polar solvents may arise in systems composed of strong acid and strong base. On the other hand, a weak acid such as phenol and a weak proton acceptor such as acetone are known to combine by the usual hydrogen bond A–H...B. In the latter case, the dipole moment usually increases only slightly because of the inductive effect or other intermolecular forces[3]. Hence we can expect the possibility of determining whether an acid-base pair is an ion pair or a hydrogen bonded complex by measuring its dipole moment. Such an investigation will be important for studying the strengths of acids and bases in non-polar solutions.

Customarily, the dissociation constants of acids and bases in aqueous solutions are respectively used as the measure of the acid and the base strength. But they are very complex in their nature, including not only the proton affinities of molecules (namely, the dissociation energies in vacuum) but also the heats of hydration and the entropy terms. On the other hand, in non-polar solvents, the energy and entropy of solvation for the ion pair formation are so small that they may be neglected in the first approximation.

Ultraviolet[4] and infrared[5] absorption measurements have also been used successfully by some authors for the study of acid-base equilibria in non-polar solvents. However, these spectroscopic methods can be applied only to compounds having absorption bands which are easily measurable and vastly affected by the formation of the ion pair. The method of dipole moment measurement has no such limitations and may give in some cases a stronger evidence of the ion-par formation.

Experimental

Measurements of the dielectric constants were made with both the resonance method and the heterodyne beat method. The apparatuses used are described elsewhere[6,7]. Densities were measured with a picnometer.

Preparation and Purification of Materials. —Pyridinium picrate was prepared by mixing the methanol solutions of purified pyridine* and picric acid, followed by recrystallization from methanol, and dried in a vacuum desiccator. Anilinium picrate was prepared from the benzene solutions of aniline and picric acid by a similar method to that described above. Phenol was purified by fractional crystallization, then fused, dried with calcium chloride and distilled under a reduced pressure. Hexamethylenetetramine was recrystallized from ethanol and dried in a vacuum desiccator. Capric acid was purified by distillation. *p*-Nitrophenol was recrystallized from a ethanol-methanol mixture and dried. Triethylamine (the reagent of the Eastman Organic Chemicals Department) was dried with sodium hydroxide and distilled. Acetic acid and trichloroacetic acid are both the guaranteed reagent of the Wako Pure Chemical Industried Ltd. The former was dried with phosphorous pentoxide and distilled, while the latter was used without further purification. Monochloroacetic acid and dichloroacetic acid were purified by distillation under a reduced pressure. Dioxane, benzene and

1) C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956); G. S. Hooper and C. A. Kraus, *J. Am. Chem. Soc.*, **56**, 2265 (1934); J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

2) A. A. Maryott, *J. Res. Nat. Bur. St.*, **41**, 1, 7 (1948).

3) H. Baba and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 3 (1951).

4) A. Nisonoff, L. P. Kuhn and R. W. Gurney, *J. Chem. Phys.*, **20**, 985 (1952); M. M. Davies and H. B. Hetzer, *J. Res. Nat. Bur. St.*, **48**, 387 (1952); M. M. Davis and E. A. McDonald, ibid., **42**, 595 (1949).

5) G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, **76**, 5211, 5248 (1954); **77**, 4474, 6206 (1955); **78**, 5802 (1956).

6) S. Nagakura and A. Kuboyama, *Repts. Inst. Sci. Technol. Univ. Tokyo*, **4**, 242 (1950).

7) K. Kozima and T. Yoshino, *J. Am. Chem. Soc.*, **75**, 166 (1953).

* This was kindly offered by Dr. T. Tamura of this Laboratory.

carbon tetrachloride were dried with sodium, phosphorous pentoxide and calcium chloride, respectively, and distilled.

Experimental Results and Method of Calculation

The results of the measurements are given in Tables I–IX, where n_a and n_b are concentrations of acids and bases in unit of mole/g. of the solution, ε is the dielectric constant and v the specific volume. x_c in Table I denotes the concentration of the salt in unit of mole fraction. For the calculation of the dipole moments, the stoichiometric formation of the acid-base complex was assumed, irrespective of whether it is an ion pair or a hydrogen bond complex, because it is known that the equilibrium constant for the hydrogen-bond formation between acid and base molecules is very great[4,8]. As for the solution where the base is present excessively, therefore, the concentration of the free base was taken as equal to $n_b - n_a$**. For the hexamethylenetetramine-phenol system only, the dissociation is not small enough to be neglected. In this case, the concentration of the complex was calculated by use of the dissociation constant of the system determined by the previous infrared spectroscopic measurement[8].

If we assume that, in dilute solutions, the distances between dipoles are so large that their interactions are negligibly small, the polarization of the solution per one gram of the solution may be expressed as follows:

$$p = (\varepsilon - 1)v/(\varepsilon + 2) = \sum_j n_j P_j \qquad (1)$$

TABLE I
PYRIDINIUM PICRATE
Solvent: dioxane. at 15°C

$x_c \times 10^4$	v	ε
0.000	0.96321	2.239
2.376	0.96256	2.277
4.340	0.96182	2.305
6.824	0.96098	2.355

$\varepsilon = 2.237 + 167.9\, x_c$
$v = 0.96326 - 3.31\, x_c$
$P_c = 2380$, $\mu = 10.43D$

TABLE II
ANILINIUM PICRATE
Solvent: dioxane. at 23°C

$n_c \times 10^5$	v	ε	P_c
0.000	0.97134	2.2265	
1.343	0.97025	2.3030	980
2.696	0.96890	2.4262	1218

P_c(average) = 1099 $\mu = 7.0D$

TABLE III
TRICHLOROACETIC ACID-TRIETHYLAMINE
Solvent: dioxane. at 20°C

$n_a \times 10^5$	$n_b \times 10^5$	v	ε	P_c
0.000	0.000	0.96771	2.2253	
0.5739	2.283	0.96818	2.3003	2130
1.856	4.774	0.96804	2.4329	1784

P_c(average) = 1957 $\mu = 9.6D$

TABLE IV
DICHLOROACETIC ACID-TRIETHYLAMINE
Solvent: dioxane. at 25°C

$n_a \times 10^5$	$n_b \times 10^5$	v	ε	P_c
0.000	0.000	0.97360	2.2258	
1.293	8.318	0.97619	2.3286	1290
2.261	14.548	0.97791	2.3953	1201
4.019	25.86	0.98124	2.5191	1375

P_c(average) = 1289 $\mu = 7.76D$

TABLE V
MONOCHLOROACETIC ACID-TRIETHYLAMINE
Solvent: dioxane (the same material as used in the above system). at 25°C

$n_a \times 10^5$	$n_b \times 10^5$	v	ε	P_c
1.714	9.800	0.97654	2.3461	1134
2.748	16.95	0.97900	2.4173	1110
4.959	34.23	0.98498	2.5610	1049

P_c(average) = 1098 $\mu = 7.15D$

TABLE VI
ACETIC ACID-TRIETHYLAMINE
Solvent: benzene. at 25°C

$n_a \times 10^5$	$n_b \times 10^5$	v	ε	P_c
0.000	0.000	1.14427	2.2724	
0.5453	1.784	1.14445	2.2826	388
1.336	3.761	1.14467	2.2943	349
2.780	8.790	1.14505	2.3206	360

P_c(average) = 366 $\mu = 3.96D$

8) H. Tsubomura *J. Chem. Phys.*, **23**, 2130 (1955).

** Barrow et al. have proposed, by the measurements of the infrared spectra of carboxylic acid-amine systems in non-polar solvents, that in the solution there are two molecular species, I and II, which have the composition of $(Acid)_2 \cdot Amine$ and $Acid \cdot Amine$, respectively. In this paper, the dipole moment of the carboxylic acid-amine complex was calculated under the assumption that all the acid molecules in the solution are converted into species II. For the dioxane solutions of triethylammonium salts of mono-, di- and tri-chloroacetic acids, this assumption seems to be valid because it is known that many carboxylic acids exist as monomers in dioxane solution[9], and under such a condition the formation of I is considered to be impossible. As for the case of acetic acid-triethylamine-benzene system, the validity of the assumption is not quite sure. In carrying out the measurement of this system, therefore, we made the concentration of triethylamine many times greater than that of acetic acid in order to increase the concentration of species II. Hence, even if the species I exists in the solution, its concentration will be small compared with the total acid concentration, and it is considered that the conclusion given later is essentially unaltered.

9) R. J. W. Le Fèvre and H. Vine, *J. Chem. Soc.*, **1938**, 1795.

TABLE VII

p-NITROPHENOL-TRIETHYLAMINE

Solvent: dioxane. at 20°C

$n_a\times10^5$	$n_b\times10^5$	v	ε	P_c
0.000	0.000	0.96825	2.2299	
0.9517	1.3826	0.96836	2.2689	721
1.1935	1.7125	0.96843	2.2786	720

P_c(average) = 721 $\mu = 5.57D$

TABLE VIII

PHENOL-HEXAMETHYLENETETRAMINE

Solvent: carbon tetrachloride. at 27°C

$n_a\times10^5$	$n_b\times10^5$	$1/v$	ε	P_c
0.000	0.000	1.58062	2.2179	
2.721	0.000	1.57852	2.2310	77.3*
2.711	2.535	1.57791	2.2402	158
2.727	1.661	1.57475	2.2364	151

P_c(average) = 155 $\mu = 2.05D$

* Molecular polarization of phenol. From it the dipole moment of phenol is calculated to be 1.55*D*.

TABLE IX

CAPRIC ACID-HEXAMETHYLENETETRAMINE

Solvent: carbon tetrachloride (the same material as used in the above system). at 27°C

$n_a\times10^5$	$n_b\times10^5$	$1/v$	ε	P_c
1.820	2.271	1.57475	2.2256	136

$\mu = 1.50D$

TABLE X

	P_E+P_A	μ
pricric acid[a]	43.0	1.55
phenol	28.0	1.55
p-nitrophenol[b]	37.2	5.0
acetic acid[c]	12.8	1.7
monochloroacetic acid[d]	17.9	2.6[d]
dichloroacetic acid[d]	23.0	2.6[d]
trichloroacetic acid[d]	28.1	2.6[d]
capric acid[e]	49.6	1.7
hexamethylenetetramine[11]	41.0	0.0
triethylamine[10]	33.7	0.8
pyridine[f]	24.0	2.2
aniline[g]	32.0	1.9

a The P_E+P_A of this compound is estimated from those of *p*-nitrobenzene, and *p*-nitrophenol. The dipole moment is taken equal to that of phenol.

b Donle and Gehrckens, *Z. phys. Chem.*, **B18**, 316 (1932).

c C. T. Zahn, *Phys. Rev.*, **37**, 1516 (1931); Wilson and Wenzke, *J. Chem. Phys.*, **2**, 546 (1934).

d Taken as equal to the moment of the ethyl ester.

e The P_E+P_A of this compound is calculated by use of the polarizations of atoms. The moment is assumed as equal to that of acetic acid.

f Leis and Curran, *J. Am. Chem. Soc.*, **67**, 79 (1945).

g Kumler and Halverstadt, ibid., **63**, 2182 (1941).

TABLE XI

Acid	Base	(Debye units) μ_{obs}	μ_s	$\Delta\mu$
picric acid	pyridine	10.43	3.4	7
picric acid	aniline	7.0	1.8	6
trichloroacetic acid	triethylamine	9.6	3.0	8
dichloroacetic acid	triethylamine	7.76	3	7
monochloroacetic acid	triethylamine	7.15	3	6.5
acetic acid	triethylamine	3.96	2.2	3
p-nitrophenol	triethylamine	5.57	5.4	0.3
capric acid	H. M. T.*	2.05	1.55	0.5
phenol	H. M. T.	1.50	1.70	−0.2

* Hexamethylenetetramine

where n_j denotes the n value of each component, and P_j is its molecular polarization. In general, there are four components in the solution: the solvent, the free acid, the free base and the complex. From Eq. 1, the molecular polarization of the complex, P_c, can be calculated, when the polarizations of the other components are known. The polarization of the solvent is derived from the measurement of the pure solvent. The P_j values of the free acid and base need not be very accurate, because their concentrations in the solution are very small. The P_j value of triethylamine was set equal to 46.6 cc. for the benzene solution[10], and to 47.2 cc. in the dioxane solution. The latter value was obtained from the measurement of ε and v of the dioxane solutions of triethylamine. For the system composed of hexamethylenetetramine and phenol, the polarization of the former was taken as

10) K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res.*, **31**, 311 (1937).

41.0 cc.[11] and that of the latter was experimentally obtained with the present sample of phenol (Table VIII).

Kraus et al.[1] stated that, for solutions of some salts with large dipole moments, the measured molecular polarization of the salt decreases rapidly with increasing concentration even in the range of the concentration of 10^{-4} mole fraction. They attributed this as due to the association of the polar salts. Maryott[2] observed, however, that the molecular polarizations of similar salts are nearly constant up to more concentrated solutions, when dioxane is used as the solvent. Also, in the present measurement with the pyridinium picrate solutions, it was found that the P_c values obtained from each solution by use of Eq. 1 agree well with that derived by the method of Halverstadt and Kumler[12]. From these facts, it may be inferred that the effect of association is negligibly small in the dioxane solutions with the range of concentration of the present measurements. In the present investigation, salts with large dipole moments are measured in the dioxane solutions, while other salts (or hydrogen bonded complexes) with smaller dipole moments, where the effect of association will be small, are measured in benzene or carbon tetrachloride solutions. The P_c values obtained by use of Eq. 1 are, therefore, considered to be a good approximation to the true P_c values. They are listed in Table II–IX. The P_c value given in Table I is that obtained by Halverstadt and Kumler's method.

The orientation polarization of the salt was calculated by subtracting from P_c the electronic and atomic polarization of the complex, which were assumed as equal to the sum of those of the free acid and base. The values used were taken from literatures and reproduced in Table X, where the dipole moments of free acids and bases are also listed. The dipole moments of the acid-base complex calculated from the orientation polarizations thus obtained are given in Table I–IX.

Discussion

If the dipole moments of the acid and base in the complex remain the same as those of the free acid and base, the dipole moment of the complex will be given by the vector sum of these two moments. Let it be called the structure moment and denoted by μ_s. Now, if the observed dipole moment of an acid-base complex is very large compared with its structure moment, the complex is conceivably an ion pair. In order to calculate the structure moments, it is assumed that none of the acid and base molecules changes the structure on the complex formation, and that the OH.....N group is on a straight line. The direction of the dipole-moment vectors of the polar molecules are estimated on the basis of the bond moment data and the consideration of the resonance moments. Based on these assumptions, the structure moments are obtained as shown in Table XI. It is readily seen that the first five systems given in Table XI have the form of the ion pair, and that the last three systems are essentially hydrogen bonded complexes.

From the theoretical point of view, the dipole moment produced by the proton transfer can be estimated by assuming the electronic structure of the ion pair as follows:

$$O^-.....H—N^+$$

where the $H—N^+$ bond is purely covalent. The O.....N distance may be taken as 2.6 Å, because the lengths of the OH.....N hydrogen bonds are in general about 2.8Å, and a slight contraction is expected in the case of the ion pair. Hence, if we assume, as a first approximation, that the positive and the negative charge are, respectively, centered at the nitrogen and the oxygen nucleus, the dipole moment arising from this proton transfer is calculated as $4.80\times10^{-10}\times2.6\times10^{-8}=12.5D$. Actually, even in the case of a complete proton transfer, the dipole moment due to the proton transfer is conceivable somewhat smaller than this value, because the electronic cloud of the two molecules would be distorted so as to decrease the strong field of the dipole produced by the transfer.

Thus we have seen that there is a large dipole moment in the ion pair directed along the OH.....N straight line with the positive end on the nitrogen atom. In Table XI, $\Delta\mu$ represents the dipole moment with the above-mentioned direction, whose magnitude is so determined that the vector sum of this and μ_s is equal to the observed moment of the complex. For the tri-*n*-butylammonium picrate, the

11) R. J. W. Le Fèvre and G. J. Rayner, *J. Chem. Soc.* **1938**, 1921.
12) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

dipole moment of which was determined by Maryott as 11.9 D, the $\Delta\mu$ value is calculated to be 9.6 D. If one assumes that this complex is a pure ion pair, then, by inspection of the $\Delta\mu$ values in Table XI, it may be confimed that pyridinium picrate, trichloroacetic acid-triethylamine complex, and dichloroacetic acid-triethylamine complex are almost complete ion pairs. As for the two systems, anilinium picrate, and monochloroacetic acid-triethylamine complex, it is recognized that the $\Delta\mu$ values are a little smaller than those for the above mentioned complexes. In regard to the arbitrariness of the calculated $\Delta\mu$ values, however, it will be rather safe to make no distinction between these five systems***.

Among the remaining four systems, acetic acid-triethylamine has an appreciable $\Delta\mu$ value. It seems that in this complex there is an "incomplete proton transfer" that may be explained by either of the following two theories. The one is that the ground state of such a complex may be represented by the resonance,

$$\text{O—H}\cdots\cdots\text{N} \rightleftarrows \text{O}^-\cdots\cdots\text{H—N}^+$$

in which the contributions of the two resonance structures have the same order of magnitude. This occurs in the cases where the potential curve for the proton in the complex has a single minimum near the center of the O.....N straight line. Another explanation is that there is a tautomeric equilibrium between the ion pair and the hydrogen bonded complex. In this case, the potential curve has two minima: one near the oxygen atom and the other near the nitrogen atom, and the proton oscillates between them. At the moment, it is difficult to decide which is the correct theory. Anyway, it may be inferred from the dipole moment that acetic acid-triethylamine complex is more like a hydrogen bonded complex than an ion pair.

Relation between the Dipole Moment and the Proton Affinity.—The energy required for the proton transfer reaction, $AH+B=A^-\cdots\cdots H—B^+$, in vacuo, is generally expressed as follows,

$$E=PA(A^-)-PA(B)+E_{ip.} \qquad (2)$$

where $PA(A^-)$ is the energy required to remove proton from the acid AH, that is, the proton affinity of the anion A^-, and $PA(B)$ is that of the base B. $E_{ip.}$ is the energy necessary for bringing the anion and cation from infinite separation to the position which they occupy in the ion pair. In the non-polar solvents, where solvation energy is small, the above formula may be applied approximately with no alteration. Assuming that $E_{ip.}$ is constant for all the acid-base pairs that have the common O...H...N groups, the energy to produce an ion pair becomes the smaller, the smaller $\{PA(A^-)-PA(B)\}$ is. $PA(A^-)$ and $PA(B)$ are, respectively, related to the acid and base strength, and, therefore, it may be interesting to compare the ability of the ion-pair formation and the dissociation constants of acid and base in aqueous solutions.

Fig. 1 was drawn under this supposition, where the two axes indicate $-\log K_a$ and $-\log K_b$ of the acid and the base of a given complex. The systems which are concluded to have the structure of the ion pair are denoted by a small circle and those which are concluded to have the structure of the hydrogen bonded complex are denoted by the symbol ×. Acetic acid-triethylamine complex is regarded to be in the intermediate state. It can be seen that there is certainly a relation

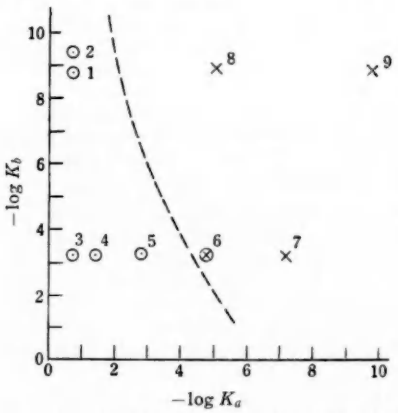

Fig. 1. Relation between the structure of acid-base complexes and the acid and base strength of their component molecules.
1. picric acid-pyridine
2. picric acid-aniline
3. trichloroacetic acid-triethylamine
4. dichloroacetic acid-triethylamine
5. monochloroacetic acid-triethylamine
6. acetic acid-triethylamine
7. *p*-nitrophenol-triethylamine
8. capric acid-hexamethylenetetramine
9. phenol-hexamethylenetetramine

*** For the case of mono- and dichloroacetic acid, the results of calculation of $\Delta\mu$ become more ambiguous owing to the possible existence of the rotational isomers.

between the ability to form ion pairs and the pK values. And the curve drawn in the figure may show roughly the limit of the pK's of acids and bases to produce ion pairs.

Shirai[13] has recently measured dipole moments of salts of dodecylamine with various carboxylic acids of the general formula $C_nH_{2n+1}COOH$ in benzene solution. The obtained values range between 1.5*D* and 2.2*D*. These values are much smaller than the dipole moment of acetic acid-triethylamine complex obtained in the present measurement, showing that the dodecylamine-carboxylic acid complexes are essentially hydrogen bonded complexes. This result may be interpreted as showing that dodecylamine is less basic than triethylamine, a result that is reasonable from the electronic theory.

In the polar solvents, the proton transfer is very much facilitated because of the large solvation energy. In the present investigation, it was observed that the dioxane solution of *p*-nitrophenol and triethylamine, which does not form the ion pair and has a faint yellow color, becomes very intensely yellow when diluted with methanol. This shows that the acid-base pair will become the ion pair or solvated ions in the more polar solvent, methanol.

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13) M. Shirai, *Sci. Pap. Coll. Gen. Educ., Univ. Tokyo*, **6**, 147 (1956).

Reactions of Active Methylene Compounds. III. A New Synthesis of 4-Hydroxy-3-phenylcoumarins

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In a previous paper[1], the author reported a preparation of 2-methoxybenzoyl-phenylacetonitriles (I), ethyl 2-methoxybenzoyl-phenylacetates (II), and 2-hydroxyphenyl benzyl ketones by ester condensation and subsequent ethanolysis and hydrolysis. In connection with it, a new synthesis of 3-aryl-4-hydroxycoumarins has been developed, and the preparation of 4-hydroxy-3-phenyl-coumarin (IVa) and its 7-methoxy-derivative (IVb) is reported in this paper.

4-Hydroxy-3-phenylcoumarins have hitherto been prepared by the following four methods:

(A) The cyclization of *o*-phenylacetoxy-derivatives of the benzoic ester with sodium at a high temperature[2].

(B) The interaction of phenols with diethyl phenylmalonate[3] or the cyclization of phenyl phenylmalonates[4] at a high temperature.

(C) The interaction of *o*-acetoxybenzoyl chloride with ethyl sodio-phenylacetate and subsequent hydrolysis[5].

(D) The cyclization of 2-hydroxyphenyl benzyl ketones by carbethoxylation with ethyl carbonate or ethyl chloroformate[6].

In the present work, the action of anhydrous aluminum chloride on the nitriles I in nitrobenzene caused demethylation and subsequent cyclization to give 4-hydroxy-3-phenylcoumarin-2-imides (III), which were also obtained by ester condensation of methyl 2-hydroxybenzoates with phenylacetonitrile. These imides III were soluble in hydrochloric acid, and seemed to be keto-forms because of their negative ferric reaction in ethanol and of their insolubility in cold aqueous alkali. The imides III

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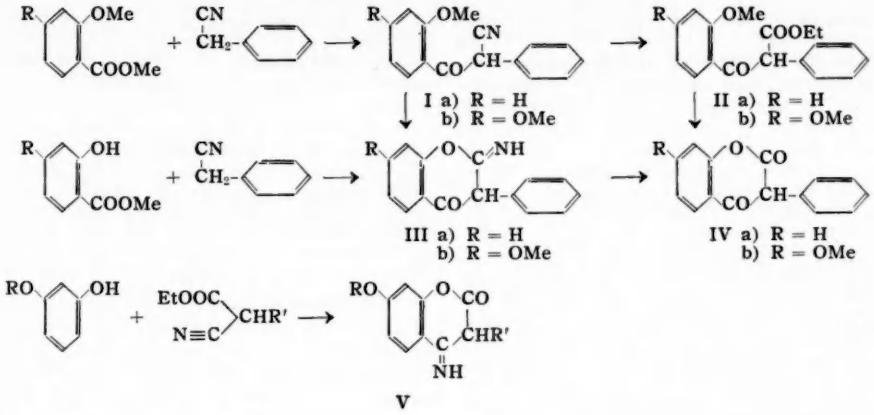
2) a) H. Pauly and K. Lockemann, *Ber.*, **48**, 32 (1915). b) M. A. Stahmann, I. Wolff and K. L. Link, *J. Am. Chem. Soc.*, **65**, 2285 (1943).

3) G. Urbain and C. Mentzer, *Bull. soc. chim.*, **11**, 171 (1944); C. Mentzer, D. Molho, and P. Vercier, *Bull. soc. chim. France*, **1949**, 749; P. Vercier, D. Molho and C. Mentzer, ibid., **1950**, 12480.

4) E. Ziegler and H. Junek, *Monatsh.*, **86**, 29 (1955); **87**, 217, 789 (1956).

5) B. S. Wildi, *J. Org. Chem.*, **16**, 407 (1951).

6) J. Boyd and A. Robertson, *J. Chem. Soc.*, **1948**, 174; A. H. Gilbert, A. McGookin and A. Robertson, ibid., **1957**, 3740.



gave 4-hydroxy-3-phenylcoumarins (IV)' when hydrolyzed with hydrochloric acid, and while salicylic acid and its 4-methoxy-derivative with aqueous sodium hydroxide. These coumarins IV were also obtained from ethyl 2-methoxybenzoyl-phenylacetates II by the action of anhydrous aluminum chloride in nitrobenzene; they were soluble in aqueous sodium carbonate, and supposed to be in keto-forms from their negative ferric reaction in ethanol.

It had been reported that the condensation of ethyl cyanoacetate with phenols according to the method of Hoesch gives 4-hydroxycoumarin-4-imides[7] (V, R=R'=H). So an attempt was made to prepare 4-hydroxy-3-phenylcoumarin-4-imides (V, R'=Ph), isomers of the imides III, from ethyl phenylcyanoacetate and resorcinol or resorcinol monomethyl ether by the Hoesch reaction, but it resulted in a failure, giving only a small amount of phenylmalonmonoamide ethyl ester[8].

Experimental[9]

4-Hydroxy-3-phenylcoumarin-2-imide (IIIa). (*a*) *From nitrile I a.*—A mixture of 0.7 g. of nitrile I a[1] and 1.5 g. of anhydrous aluminum chloride in 5 cc. of nitrobenzene was heated for two hours on a steam bath. The cooled solution was treated with water, and nitrobenzene was driven off by steam distillation. The residual aqueous mixture was extracted with ether, and the ethereal solution was then extracted with dilute hydrochloric acid. The acid aqueous solution was made alkaline with sodium bicarbonate, and the solid product which separated was recrystallized from ethanol. Colorless microcrystals, m. p. 219.5~220.5°. Yield 0.2 g., identical with the other sample from (b).

(*b*) *By ester condensation.*—To a suspension of dry sodium ethoxide (from 2 g. of sodium) in 50 cc. of absolute benzene, a mixture of 6.5 g. of methyl 2-hydroxybenzoate and 5 g. of phenylacetonitrile was added, and the mixture was heated at about 100° on an oil bath for four hours while most of benzene was driven off with the ethanol produced. Dilute hydrochloric acid was added to the well-cooled resulting mixture, which was extracted with ether. Ether and the unchanged starting materials were driven off by steam distillation. The residual aqueous mixture was treated as before to give the product, colorless microcrystals, m. p. 223~4°, yield 1.5 g.

Anal. Found: C, 76.03; H, 4.97; N, 5.40. Calcd. for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.67; N, 5.90%.

When 2 g. of sodium hydride was used instead of dry sodium ethoxide, the yield was 1.3 g., m. p. 219~220°, from 5 g. of methyl salicylate and 4 g. of phenylacetonitrile.

4-Hydroxy-3-phenylcoumarin (IVa). (*a*) *From imide III a*—A solution of 0.5 g. of imide III a in 10 cc. of dilute hydrochloric acid (1 : 1) was heated for three hours on a steam bath. A crystalline product separated from the warm solution was collected and recrystallized from ethanol to give the product in colorless needles, m. p. 231~2°, yield 0.25 g. The reported melting point is 230°[4], 234~5°[2b], 236°[2a], 237~8°[5], and 240°C[3].

Anal. Found: C, 75.41; H, 4.43. Calcd. for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23%.

(*b*) *From ester II a.*—A mixture of 0.9 g. of ester II a[1] and 2 g. of anhydrous aluminum chloride in 5 cc. of nitrobenzene was heated for one and a half hours on a steam bath. Water was added to the cooled solution, and nitrobenzene was driven off by steam distillation. The residual aqueous mixture was extracted with ether, and the ethereal solution was then extracted with aqueous sodium hydroxide. The soild product separated from the alkaline solution by acidification was purified from ethanol. Colorless needles,

7) A. Sonn. *Ber.*, **50**, 1292 (1917); K. H. Bauer and F. Schoder, *Arch. Pharm.*, **259**, 53 (1921); cf. E. Ziegler, G. Wildtgrube and M. Junek, *Monatsh.*, **88**, 164 (1957).
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9) All melting points are uncorrected.

m. p. 229~230°, yield 0.5g., identical with the other sample from (a).

4-Hydroxy-7-methoxy-3-phenylcoumarin-2-imide (III b). (*a*) *From nitrile I b.*—From 1 g. of nitrile I b[1] and 1.9 g. of anhydrous aluminum chloride in 5 cc. of nitrobenzene, 0.2 g. of the compound was obtained by the same operation described before, colorless microcrystals, m. p. 232~232.5° (from ethanol).

Anal. Found: C, 71.52; H, 5.04; N, 5.42. Calcd. for $C_{16}H_{13}O_3N$: C, 71.90; H, 4.90; N, 5.24%.

(*b*) *By ester condensation.*—To a suspension of dry sodium ethoxide (from 0.6 g. of sodium) in 50 cc. of absolute benzene, a mixture of 2 g. of methyl 2-hydroxy-4-methoxybenzoate and 1.4 g. of phenylacetonitrile was added, and the mixture was treated as before to give 0.2 g. of the product, m. p. 230~1°, identical with the other sample from (a). When 0.3 g. of sodium hydride was used instead of dry sodium ethoxide, the yield was 0.1 g., m. p. 229~230°, from 1.2 g. of ester and 0.8 g. of nitrile.

4-Hydroxy-7-methoxy-3-phenylcoumarin (IV b). (*a*) *From imide III b.*—From 0.1 g. of imide III b, 40mg. of the compound was obtained by the same operation described before, colorless microcrystals, m. p. 196~7° (form dilute ethanol), identical with the other sample from (b).

(*b*) *From ester II b.*—From 0.4 g. of ester II b[1] and 0.9 g. of anhydrous aluminum chloride, 50 mg. of the compound was obtained by the same operation described before, m. p. 196~7°. The reported melting point is 202°[3] and 204°[6].

Anal. Found: C, 71.33; H, 4.62. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51%.

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A New Viscosity Relationship in a Wide Concentration Range of Aqueous Solutions of Potassium Chloride

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Viscosity of strong electrolytes in dilute solutions conformed to an equation given on experimental basis by Jones and Dole[1] and Joy and Wolfenden[2]. This equation fails at higher concentrations. So far no equation satisfactorily explained the quantitative relationship between viscosity and concentration in the entire range from infinite dilution up to saturation. In a recent[3] systematic study by us, of electrical conductance of highly concentrated solutions of strong electrolytes up to saturation, we have derived a new concept of concentration and a modified viscosity term. In brief, the following is the basis of the new formulations.

A new concept of concentration.—Let

$$P = f(X) \qquad (1)$$

represent the physical property of a solution at a given temperature for a given solvent as a function of 'X', the mole fraction concentration of the solute. When we compare the physical property 'P' of solutions of different solutes in the same solvent, it is clear that in equation (1) 'X' can not have all possible values from zero to unity. For each electrolyte 'X' can vary from the common zero limit in all cases to the saturation limit at which the mole-fraction of the solute is not unity. Further the mole-fraction concentration at saturation is different for different electrolytes in the same solvent. If 'X' values vary in an identical range, the 'P' values of different salt solutions will be comparable at the same temperature. In other words, in the extreme limit of saturation, for different salt solutions the 'X' values must be such that they tend to an identical limit at which the 'P' values in their limit will be comparable even though they will not be identical. Therefore there is need for a new concept

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1) G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).
2) W. E. Joy and J. H. Wolfenden, *Proc. Roy. Soc.* (London), **A134**, 413 (1931).
3) C. V. Suryanarayana and V. K. Venkatesan, *Nature*, **178**, 1461 (1956).

of concentration (X^1) such that, at a given temperature, its value varies between the same limits for different electrolyte solutions. We may write

$$P = f(X^1) \qquad (2)$$

such that 'X^1' is the ratio of the mole-fraction of the solute at any given molal concentration to that at saturation at the same temperature. Such a ratio should tend to unity at saturation for all solutions at all temperatures irrespective of the nature of the solute and the solvent. This ratio of mole-fractions, was called by us the "concentration potential" (C_p). Now it is clear that a given physical property of a solution plotted against its "concentration potential" will be a curve worthy of comparison with similar ones for different electrolytes in a given solvent. The concentration potential newly conceived herein is a truly thermodynamic concept of concentration dependent only on the initial and final states of stability of a solution and independent of any arbitrary scale of concentration or the nature of both the solvent and the solute.

A new concept of viscosity.—So far in literature the relative viscosity of a solution has been relative to the solvent and our modification consists in making it relative to that at saturation at the same temperature. This modified viscosity term (η_p), as with the concentration potential, will tend to a maximum of unity at saturation for all electrolyte solutions.

Some previous workers[4~20] collected viscosity data for potassium chloride solutions in different ranges of concentrations at a few temperatures. We have measured viscosity of potassium chloride solutions from 1.00 molal to saturation, at temperatures of 30 to 55°C.

Experimental

All solutions were made by weighing water and the required amount of solute to make a certain wanted molal concentration. A 100 cc. pyrex beaker was weighed and the process repeated after adding about 50 cc. of water. Exactly the required amount of a salt was weighed into the beaker. After gentle stirring of the solution the whole of it was transferred and kept in a well-stoppered 250 cc. pyrex bottle. This solution was used for finding the viscosity and density. All solutions except at saturation were thus made so that the concentration was independent of volume. The potassium chloride used was of guaranteed quality. Viscosity measurements were made using an Ostwald viscometer kept in a Gallenkamp b-12210 thermostat provided with a glass tank and giving an accuracy ±0.05°C. At saturation, viscosity determination required great care and repeated verification. A pyrex beaker containing the saturated solution in equilibrium with the undissolved salt was kept stirred continuously by a mechanical stirrer. After attainment of equilibrium an aliquot amount of the saturated solution was sucked through a tube plugged with cotton wool and attached to a pipet. The pipet itself was kept at the same temperature of the thermostat to avoid crystallization of the saturated solution. Soon after withdrawing into the pipet the glass-tube stuffed with cotton wool was quickly disconnected and the solution was transferred into the viscometer. After sufficient repetitions the whole technique could be mastered.

Density determination.—Density was determined in each case using the density bottle whose volume was ascertained by knowing the weight of water filling it at a known temperature and making use of exact density of water at the same temperature from tables given in Lange[21]. The density of the saturated solution was determined by weighing the volume of solution transferred by a calibrated pipet.

Solubility data of each salt at different temperatures were obtained from Seidell's "Solubilities of Organic and Inorganic Compounds"[22]. Results obtained are given in Table I.

Discussion

Figs. 1 and 2 show plots of $\log \eta_p$ vs. C_p at each temperature. At temperatures of 35, 40, 45, 50 and 55°C the plots are straight lines. Only at 30°C the plot though not a straight line, is made up of

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TABLE I

Temp. °C	Molality	C_p	Relative viscosity water=1	η_p	Temp. °C	Molality	C_p	Relative viscosity water=1	η_p
30	1.00	0.2156	1.010	0.8814	45	1.000	0.1950	1.024	0.8307
	1.50	0.3206	1.021	0.8910		1.500	0.2900	1.046	0.8484
	2.00	0.4236	1.028	0.8973		2.000	0.3832	1.058	0.8582
	2.50	0.5249	1.035	0.9033		2.500	0.4747	1.086	0.8810
	3.00	0.6244	1.046	0.9128		3.000	0.5650	1.104	0.8954
	3.50	0.7226	1.064	0.9285		3.500	0.6536	1.125	0.9124
	4.00	0.8189	1.079	0.9417		4.000	0.7406	1.148	0.9311
	4.50	0.9128	1.093	0.9539		4.500	0.8624	1.170	0.9491
	4.963	1.0000	1.145	1.0000		5.540	1.0000	1.233	1.0000
35	1.00	0.2079	1.014	0.9419	50	1.00	0.1895	1.034	0.8136
	1.50	0.3091	1.020	0.8800		1.50	0.2819	1.059	0.8333
	2.00	0.4088	1.022	0.8816		2.00	0.3727	1.076	0.8468
	2.50	0.5064	1.049	0.9048		2.50	0.4617	1.104	0.8686
	3.00	0.6027	1.060	0.9145		3.00	0.5494	1.122	0.8828
	3.50	0.6971	1.077	0.9315		3.50	0.6357	1.147	0.9024
	4.00	0.7900	1.103	0.9515		4.00	0.7202	1.173	0.9230
	4.50	0.8812	1.119	0.9651		4.50	0.8035	1.195	0.9404
	5.164	1.0000	1.159	1.0000		5.714	1.0000	1.271	1.0000
40	1.00	0.2005	1.018	0.8486	55	1.00	0.1841	1.039	0.7943
	1.50	0.2985	1.039	0.8662		1.50	0.2738	1.059	0.8098
	2.00	0.3945	1.044	0.8706		2.00	0.3617	1.081	0.8266
	2.50	0.4889	1.074	0.8958		2.50	0.4483	1.114	0.8517
	3.00	0.5817	1.089	0.9082		3.00	0.5335	1.135	0.8680
	3.50	0.6730	1.105	0.9212		3.50	0.6172	1.161	0.8880
	4.00	0.7628	1.130	0.9423		4.00	0.6993	1.188	0.9086
	4.50	0.8507	1.148	0.9572		4.50	0.7803	1.214	0.9283
	5.365	1.0000	1.199	1.0000		5.902	1.0000	1.308	1.0000

TABLE II

Temp. °C	Cons. A: Expt.	Cons. A: Extrapolated	Cons. A: % deviation	Const. B
30	0.8736	0.8710 (Ist line)	−0.3	0.03390
		0.8426 (IInd line)	—	0.05881
35	0.8630	0.8670	+0.4	0.07138
40	0.8339	0.8189	−1.8	0.07922
45	0.8112	0.8128	+0.2	0.09072
50	0.7868	0.7769	−1.27	0.10380
55	0.7647	0.7516	−1.7	0.11880

two non-collinear straight lines intersecting at a point corresponding to 2.336 molal. Therefore, in general the variation of η_p with concentration potential may be represented by the exponential equation

$$\eta_p = A\, e^{BC_p} \qquad (3)$$

the constants A and B being dependent upon temperature. At 30°C and below potassium chloride solutions are known to exhibit negative viscosity. Even then, the above exponential equation is applicable at 30°C, the non-colliner straight lines signifying only variations in constants A and B of the above equation.

It is clear from equation (3) that at infinite dilution C_p is zero and η_p equals to A. In other words A is the ratio of the viscosity of water to that of the solution when saturated with potassium chloride at a given temperature. This value of A

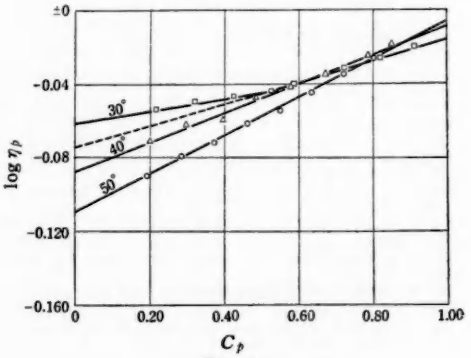

Fig. 1.

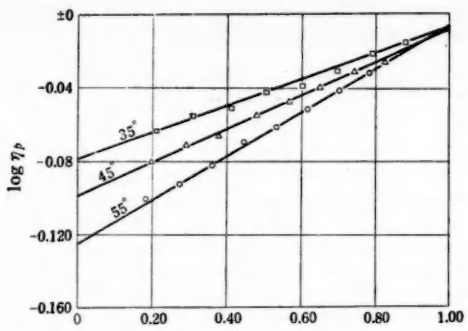

Fig. 2.

could be easily found from the experimental determination of the viscosity of the solution at saturation. Also by plotting at each temperature $\log \eta_p$ against C_p, by extrapolating $C_p = 0$ and by a small mathematical transformation of the value of the intercept we can obtain the value of 'A'. Thus in Table II in addition to the constant B at different temperatures the extrapolated and the experimentally determined values of 'A' are compared side by side. The percentage deviation between the extrapolated and the calculated values ranges from 0.2 to 1.80. Considering the difficulties involved in precision measurements of viscosity of saturated solutions and errors involved in extrapolation of values quite small in magnitude, the agreement is quite within limits. The constant 'B' may be probably related to the properties of the solute and requires further elucidation in furture.

Summary

A systematic investigation of viscosity from 1.00 m. to saturation of aqueous solutions of potassium chloride at temperatures of 30, 35, 40, 45, 50 and 55°C has been made. New concepts of concentration and viscosity have been defined. At a given molal concentration the ratio of the mole-fraction at that concentration to that at saturation at the same temperature has been called concentration potential C_p. The newly defined viscosity term η_p is the ratio of the viscosity at a given concentration to that at saturation at the same temperature. Using these two quantities the variation of viscosity with concentration could be expressed for potassium chloride solutions by a simple exponential equation:

$$\eta_p = A\, e^{BC_p}$$

where A and B are constants.

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*Ion Exchange in Concentrated Solutions. III. Magnesium Chloride-Hydrochloric Acid and Aluminum Chloride-Hydrochloric Acid Systems**

By Hitoshi OHTAKI and Kazuo YAMASAKI

(Received January 6, 1958)

The ion-exchange equilibria in sodium chloride-hydrochloric acid[1], lithium chloride-hydrochloric acid[1] and beryllium chloride-hydrochloric acid[2] systems were studied in the previous reports. In the present report, the equilibria in magnesium chloride-hydrochloric acid and aluminum chloride-hydrochloric acid systems are investigated.

* Read before the 10th Annual Meeting of the Chemical Society of Japan held at Tokyo in April, 1957.

1) H. Kakihana, N. Maruichi and K. Yamasaki, *J. Phys. Chem.*, **60**, 36 (1956).

2) H. Ohtaki and K. Yamasaki, This Bulletin, **31**, 6 (1958).

Experimental

The Resin.—The resin used was Dowex 50-X8 (hydrogen form) of mesh size 30~80 obtained by wet screening. It was dried at 40°C. The water content of the resin used was determined from

the weight decrease on drying at 110°C. It was about 16.58~20.62%, i. e., 0.20~0.23 ml. per gram resin used for magnesium chloride-hydrochloric acid system and 9.82%, i. e., 0.11 ml. for that used for aluminum chloride-hydrochloric acid system. The amount of the resin used in one batch experiment was 3.6 g. The exchange capacity of the resin used was determined in each series of experiments.

Reagents.—Magnesium chloride of reagent grade was used without purification. Aluminum chloride was dissolved in water to prepare a concentrated solution. After adding hydrochloric acid, the concentrated solution was cooled by the freezing mixture and the stream of dried hydrogen chloride was passed through it. White crystals of aluminum chloride precipitated. After filtration the crystals were washed with cold concentrated hydrochloric acid and then dissolved in water containing a small amount of hydrochloric acid to prevent hydrolysis. This solution was mixed with hydrochloric acid to prepare sample solutions.

Procedure. — All the procedures used for determination of the adsorbed water are similar to those used in the previous studies[1,2]. Mixtures of 0.1~5 N magnesium chloride and 0~11 N hydrochloric acid and those of 0.2~0.9 N aluminum chloride and 0.5~11 N hydrochloric acid were used. In the concentration range lower than 0.5 N of hydrochloric acid the hydrolysis of aluminum chloride occurred, while too much presence of hydrochloric acid caused to crystallize some part of aluminum chloride. Therefore the concentration of hydrochloric acid was maintained lower than 3 N when that of aluminum chloride was 0.9 N.

The concentration of the magnesium ion was determined by titration with 0.02 and 0.001M ethylenediaminetetraacetate solution using Eriochrome Black T as indicator[3]. The concentration of the aluminum ion was titrated by 0.03 M ethylenediaminetetraacetate solution with Chrome Azurol S as indicator[4]. Hydrogen ion concentrations of these solutions were determined by titration with 0.1 N barium hydroxide. Brom Cresol Purple (pH of the color change: 5.2~6.8) was used as indicator for the magnesium chloride-hydrochloric acid system, while Methyl Yellow (pH of the color change: 2.9~4.0) was used for the aluminum chloride-hydrochloric acid system, because aluminum chloride was hydrolyzed in higher pH range.

Results and Discussion

1) Water in the Resin. — The amount of water adsorbed by the resin which was in contact with the external solution was estimated indirectly by measuring the amounts of the hydrogen ion before and after the ion-exchange equilibrium and using the following equation[1,2]:

$$A' = \frac{(H^+)_S \cdot V + [H^+]_Q + [H^+]_R - [H^+]_O - E}{(H^+)_S} \quad (1)$$

In equation (1), A' denotes the adsorbed water in the resin at equilibrium and round and square brackets denote the concentration and the amount of ions, respectively. V represents the volume of the original solution taken up in one batch experiment (30 ml.); subscripts S, Q, R and O denote the external solution at equilibrium, the quasi-exchange phase*, the resin phase at equilibrium and the original solution, respectively[1,2]; E represents the total exchange capacity of the resin used. When the original water content of the resin used is represented by A'', the total amount of the water in the resin is

$$A = A' + A''. \quad (2)$$

Amounts of the water per gram of dried resin thus determined are given in Tables I and II together with other data. As clearly shown in these tables values of the water in the resin for the aluminum chloride-hydrochloric acid system are generally smaller than those for beryllium chloride-hydrochloric acid[2] and magnesium chloride-hydrochloric acid systems. It is known that the larger the charge of the ion exchanged in the resin phase is, the more the resin shrinks. The experimental data shown in Tables I and II are consistent with this fact.

2) Ionic Species in the External Solution and the Resin.—As shown in Tables I and II, the sum of the amounts of hydrogen ion, $[H^+]_R$ and metal ion $[Mg^{2+}]_R$ or $[Al^{3+}]_R$ in the resin phase is larger than the total exchange capacity of the resin used. These discrepancies are supposed to have been caused by the formation of complexes* such as $MgCl^+$, $AlCl^{2+}$ or $AlCl_2^+$ which exchange with hydrogen ions. The existence of such complexes containing chlorine in the resin phase is verified by the detection of a minute amount of chloride ion in the solution eluted from the resin by sodium nitrate even after washing the resin thoroughly with water.

3) G. Schwarzenbach, "Die komplexometrische Titration", F. Enke Stuttgart, 2nd Ed. p. 54 (1956).
4) M. Theis, *Z. anal. Chem.*, **114**, 106 (1955).

* This phase consists of two kinds of solution: one is the solution which adheres to the surface of resin particles and the other is the solution which penetrates into the resin without being exchanged at the time of the exchange equilibrium. See References 1 and 2.

TABLE I

A PART OF THE DATA FOR THE $MgCl_2$-HCl SYSTEM.

(1) Concentration of the original solution of $MgCl_2$, $(Mg^{2+})_O = 0.11$ N; total exchange capacity of the resin, $E = 15.00$ meq.

$(H^+)_O$	0.32	0.65	1.09	1.93	4.31	8.76	N
$(H^+)_S$	0.41	0.75	1.21	2.04	4.44	8.82	N
$(Mg^{2+})_S$	0.00_8	0.02_1	0.04	0.07	0.09	0.09	N
$[H^+]_Q$	0.24	0.56	1.08	1.56	5.11	11.42	meq.
$[Mg^{2+}]_Q$	0.09	0.10	0.04	0.02	0.02	0.06	meq.
$[H^+]_R$	12.89	13.50	13.86	14.30	14.72	14.89	meq.
$[Mg^{2+}]_R$	3.45	2.75	2.37	1.40	0.75	0.43	meq.
$[H^+]_R+[Mg^{2+}]_R$	16.34	16.25	16.23	15.70	15.47	15.32	meq.
water in the resin, *A*.	0.90	1.12	1.13	0.89	0.84	0.69	ml./g. dry resin.

(2) $(Mg^{2+})_O = 0.29$ N, $E = 15.00$ meq.

$(H^+)_O$	0.00	0.61	2.06	3.09	5.12	8.18	N
$(H^+)_S$	0.20	0.79	2.24	3.23	5.24	8.25	N
$(Mg^{2+})_S$	0.00_9	0.11	0.23	0.26	0.28	0.28	N
$[H^+]_Q$	0.19	0.70	2.06	3.72	5.81	11.96	meq.
$[Mg^{2+}]_Q$	0.01	0.01	0.03	0.02	0.02	0.08	meq.
$[H^+]_R$	9.48	11.08	13.40	14.05	14.37	14.52	meq.
$[Mg^{2+}]_R$	9.03	6.53	2.86	2.01	1.08	0.98	meq.
$[H^+]_R+[Mg^{2+}]_R$	18.51	17.61	16.26	16.06	15.45	15.50	meq.
water in the resin, *A*.	1.27	1.12	1.10	0.93	0.76	0.74	ml./g. dry resin.

(3) $(Mg^{2+})_O = 0.50$ N, $E = 14.08$ meq.

$(H^+)_O$	0.00	1.02	3.04	5.11	8.17	10.78	N
$(H^+)_S$	0.29	1.21	3.17	5.21	8.15	10.51	N
$(Mg^{2+})_S$	0.07	0.31	0.45	0.48	0.48	0.47	N
$[H^+]_Q$	0.19	1.09	3.44	7.31	10.73	14.01	meq.
$[Mg^{2+}]_Q$	0.01	0.03	0.04	0.11	0.20	0.24	meq.
$[H^+]_R$	5.95	10.15	12.63	13.27	13.60	13.59	meq.
$[Mg^{2+}]_R$	13.13	6.91	2.63	1.86	1.39	1.42	meq.
$[H^+]_R+[Mg^{2+}]_R$	19.08	17.06	15.26	15.13	14.99	15.01	meq.
water in the resin, *A*.	1.05	1.04	0.92	0.91	0.66	0.43	ml./g. dry resin.

(4) $(Mg^{2+})_O = 1.00$ N, $E = 14.08$ meq.

$(H^+)_O$	0.00	1.02	3.02	5.17	8.24	10.37	N
$(H^+)_S$	0.36	1.29	3.20	5.29	8.25	10.13	N
$(Mg^{2+})_S$	0.48	0.74	0.91	0.96	0.97	0.99	N
$[H^+]_Q$	0.52	1.62	4.37	8.01	13.46	14.01	meq.
$[Mg^{2+}]_Q$	0.05	0.07	0.08	0.30	0.63	0.58	meq.
$[H^+]_R$	3.54	8.11	11.36	12.53	13.02	13.05	meq.
$[Mg^{2+}]$	16.96	10.00	4.90	3.14	2.51	2.51	meq.
$[H^+]_R+[Mg^{2+}]_R$	20.50	18.11	16.26	15.67	15.53	15.56	meq.
water in the resin, *A*.	1.09	1.06	1.01	0.86	0.86	0.46	ml./g. dry resin.

(5) $(Mg^{2+})_O = 2.99$ N, $E = 14.08$ meq.

$(H^+)_O$	0.27	0.80	2.53	7.09	N
$(H^+)_S$	0.66	1.14	2.77	7.13	N
$(Mg^{2+})_S$	2.55	2.65	2·81	2.90	N
$[H^+]_Q$	1.92	2.80	5.75	13.20	meq.
$[Mg^{2+}]_Q$	1.09	0.69	0.48	1.98	meq.
$[H^+]_R$	2.33	3.96	7.34	10.66	meq.
$[Mg^{2+}]_R$	18.67	16.47	11.36	6.26	meq.
$[H^+]_R+[Mg^{2+}]_R$	21.00	20.43	18.70	16.92	meq.
water in the resin, *A*.	1.16	1.12	1.06	0.79	ml./g. dry resin.

(6) $(Mg^{2+})_O$=4.96 N, E=14.08 meq.

$(H^+)_O$	0.00	0.80	5.13	N
$(H^+)_S$	0.41	1.14	5.26	N
$(Mg^{2+})_S$	4.58	4.72	4.92	N
$[H^+]_Q$	1.39	3.60	10.69	meq.
$[Mg^{2+}]_Q$	3.62	3.15	2.71	meq.
$[H^+]_R$	1.30	2.91	8.11	meq.
$[Mg^{2+}]_R$	20.48	18.02	9.98	meq.
$[H^+]_R+[Mg^{2+}]_R$	21.78	20.93	18.09	meq.
water in the resin, A.	1.06	1.17	0.82	ml./g. dry resin.

TABLE II

A PART OF THE DATA FOR THE $AlCl_3$-HCl SYSTEM.*

(1) Concentration of the original solution of $AlCl_3$, $(Al^{3+})_O$=0.18 N; total exchange capacity of the resin, E=16.69 meq.

$(H^+)_O$	1.07	2.17	3.23	5.30	8.47	11.65	N
$(H^+)_S$	1.25	2.37	3.37	5.44	8.53	11.43	N
$(Al^{3+})_S$	0.03	0.07	0.12	0.14	0.14	0.15	N
$[H^+]_Q$	1.13	2.84	4.69	8.33	16.19	20.26	meq.
$[H^+]_R$	13.49	14.61	15.17	15.54	15.68	15.70	meq.
$[Al^{3+}]_R$	3.99	2.66	2.41	1.28	1.33	1.28	meq.
$[H^+]_R+[Al^{3+}]_R$	17.48	17.27	17.58	16.82	17.01	16.98	meq.
water in the resin, A.	0.95	0.85	0.78	0.76	0.72	0.52	ml./g. dry resin.

(2) $(Al^{3+})_O$=0.52 N, E=16.69 meq.

$(H^+)_O$	0.38	0.65	1.12	2.17	5.01	10.66	N
$(H^+)_S$	0.72	0.98	1.41	2.42	5.20	10.59	N
$(Al^{3+})_S$	0.12	0.14	0.26	0.39	0.49	0.39	N
$[H^+]_Q$	0.74	1.13	1.49	3.38	8.66	18.80	meq.
$[H^+]_R$	7.87	8.77	10.30	12.80	14.78	15.19	meq.
$[Al^{3+}]_R$	14.23	11.76	9.35	5.18	2.03	1.25	meq.
$[H^+]_R+[Al^{3+}]_R$	22.10	20.53	19.65	17.98	16.81	16.44	meq.
water in the resin, A.	0.89	0.92	0.83	0.86	0.74	0.43	ml./g. dry resin.

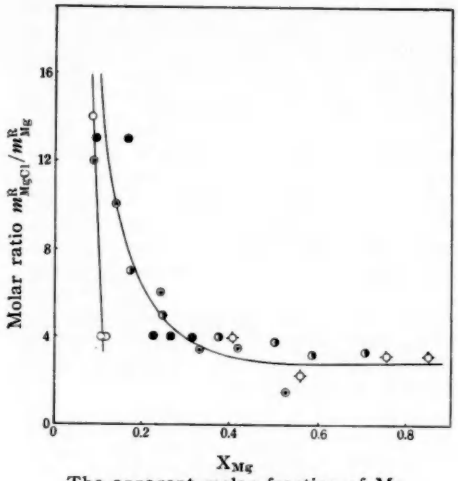
(3) $(Al^{3+})_O$=0.77 N, E=16.69 meq.

$(H^+)_O$	0.45	1.17	2.16	7.41	N
$(H^+)_S$	0.82	1.44	2.39	7.64	N
$(Al^{3+})_S$	0.29	0.51	0.66	0.68	N
$[H^+]_Q$	1.07	2.30	3.87	13.47	meq.
$[H^+]_R$	6.62	9.34	11.96	14.80	meq.
$[Al^{3+}]_R$	14.59	11.36	7.07	1.59	meq.
$[H^+]_R+[Al^{3+}]_R$	21.21	20.70	19.03	16.39	meq.
water in the resin, A.	1.23	0.73	0.87	0.84	ml./g. dry resin.

(4) $(Al^{3+})_O$=0.90 N, E=16.69 meq.

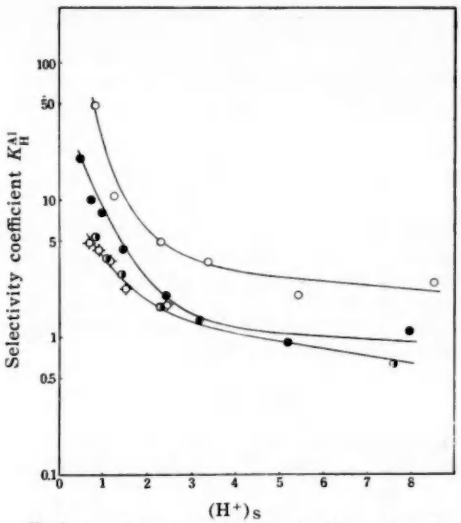
$(H^+)_O$	0.79	1.26	2.21	N
$(H^+)_S$	1.14	1.58	2.48	N
$(Al^{3+})_S$	0.58	0.76	0.78	N
$[H^+]_Q$	1.50	2.06	3.39	meq.
$[H^+]_R$	6.99	8.89	11.29	meq.
$[Al^{3+}]_R$	15.50	12.10	7.88	meq.
$[H^+]_R+[Al^{3+}]_R$	22.49	20.99	19.17	meq.
water in the resin, A.	1.04	0.87	0.88	ml./g. dry resin.

* The amount of Al^{3+} ion in the quasi-exchange phase is too small to be determined in all cases. Therefore values of $[Al^{3+}]_Q$ are not given in this table.



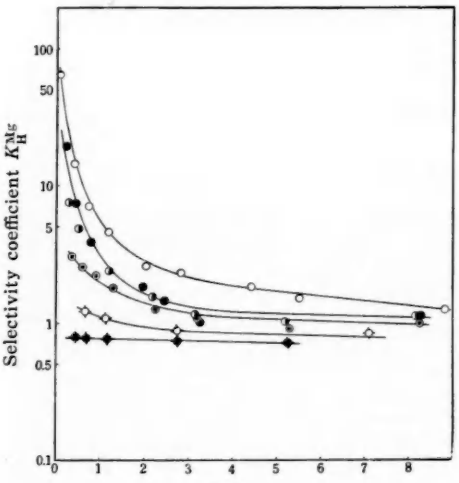
The apparent molar fraction of Mg ion in the resin

Fig. 1. Relation between molar ratio of $MgCl^+$ to Mg^{2+} in the resin and the apparent molar fraction of Mg ion in the resin.
○ 0.1 ● 0.3 ⊙ 0.5 ◑ 1.0
◇ 5.0 N $MgCl_2$



Hydrogen ion concentration in the external solution at equilibrium

Fig. 3. Selectivity coefficients of $AlCl_3$ −HCl system plotted against $(H^+)_S$.
○ 0.18 ● 0.53 ◑ 0.77
◇ 0.90 N $AlCl_3$



Hydrogen ion concentration in the external solution at equilibrium

Fig. 2. Selectivity coefficients of $MgCl_2$ −HCl system plotted against $(H^+)_S$.
○ 0.1 ● 0.3 ◑ 0.5 ⊙ 1.0
◇ 3.0 ◆ 5.0 N $MgCl_2$

Amounts of Mg^{2+} and $MgCl^+$ ions in the resin phase can be readily calculated from the values of E, $[H^+]_R$ and $[Mg^{2+}]_R$ provided that no other complexes are formed. In Fig. 1 values of the molar ratio of $MgCl^+$ to Mg^{2+} ion in the resin m^R_{MgCl}/m^R_{Mg} are plotted against the apparent molar fraction of magnesium ion in the resin, X_{Mg}*. The molar ratio increases as X_{Mg} decreases. Thus, in the range of lower concentration of magnesium chloride and at the same time of higher concentration of hydrochloric acid, magnesium in the resin phase consists almost entirely of $MgCl^+$, and it is possible that a large part of magnesium present in the external solution also forms the chloro-complex $MgCl^+$.

In Fig. 2 values of selectivity coefficient of magnesium calculated after the formula

$$K^{Mg}_H = \frac{(H^+)_S\{[Mg^{2+}]_Q + [Mg^{2+}]_R\}}{(Mg^{2+})_S\{[H^+]_Q + [H^+]_R\}} \quad (3)$$

are plotted against $(H^+)_S$, the hydrogen ion concentration of the external solution. In the range of higher values of $(H^+)_S$, as already described, the ionic species predominant is considered to be $MgCl^+$. Consequently the selectivity coefficient thus calculated represents that of the exchange

* Hydroxo-complexes are formed with difficulty in such a strong acidic system as the resin phase concerned. Actually water may be coordinated to these ions in forming $[Mg(OH_2)_5Cl]^{2+}$, $[Al(OH_2)_5Cl]^{2+}$, $[Al(OH_2)_4Cl_2]^+$.

* $X_{Mg} = \frac{1}{2}[Mg^{2+}]_R/\{[H^+]_R + \frac{1}{2}[Mg^{2+}]_R\}$

system of $MgCl^+$—H^+ rather than that of Mg^{2+}—H^+ system.

The selectivity coefficient of the aluminum chloride-hydrochloric acid system was calculated by the similar formula as (3):

$$K_H^{Al}=\frac{(H^+)_S\{[Al^{3+}]_Q+[Al^{3+}]_R\}}{(Al^{3+})_S\{[H^+]_Q+[H^+]_R\}} \quad (4)$$

These data are plotted against $(H^+)_S$ in Fig. 3. In this system it is difficult to estimate the amount of individual species of aluminum like Al^{3+}, $AlCl^{2+}$ or $AlCl_2^+$ in the similar way as in the magnesium chloride-hydrochloric acid system.

Summary

Ion-exchange equilibria in the concentrated solutions of magnesium chloride-hydrochloric acid and aluminum chloride-hydrochloric acid system were studied. Amounts of the water present in the resin at equilibrium were estimated for these systems. In the magnesium chloride-hydrochloric acid system a large part of magnesium in the resin exists as $MgCl^+$ at equilibrium when the concentration of hydrochloric acid is high. Selectivity coefficients of magnesium chloride-hydrochloric acid and of aluminum cholride-hydrochloric acid systems were calculated.

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Selective Oxidation of Allylic Alcohols with Active N-Halogen Compounds. I. Synthesis of Testosterone and of 4-Pregnen-20β-ol-3-one[1]

By Ken-ichi MORITA

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Treatment of allylic, propargylic and benzylic alcohol with manganese dioxide at room temperature has been shown to be an effective method for the selective oxidation of these alcohols[2]. It seems necessary, however, to search other reagents for the reactions, since recent studies indicate that in some cases even under mild conditions the oxidation of saturated primary and secondary alcohols may occur[3].

Lecompte and his colleagues[4] reported the oxidation reactions of a large number of alcohols containing benzene rings with *N*-bromoacetamide. It should be noted that hydroxyl groups in positions adjacent to the aromatic systems in the alcohols are easily oxidized to carbonyl groups, whereas hydroxyl groups in other positions are unaffected under similar conditions. Thus, 1-hydroxy-1, 2, 3, 4-tetrahydronaphthalene[4a], benzhydrol and benzyl alcohol[4b] are easily oxidized to corresponding carbonyl compounds, while the oxidation of 2-hydroxy-1,2,3,4-tetrahydronaphthalene[4a], 1,3-diphenyl-2-propanol and 2-phenylethanol[4b] does not occur. Lieberman and Fukushima[5] reported that the reaction of 5-cholestene-3β, 4β, 7α-trial 3-monoacetate with *N*-bromoacetamide gave 5-cholestene-3β,4β-diol-7-one 3-monoacetate in a quantitative yield*. These observations suggest that the active *N*-halogen compounds such as *N*-bromoacetamide may be effective

1) Steroids Part XXII; Part XXI, This Bulletin, **31**, 347 (1958).

2) G. Rosenkranz et al., *J. Chem. Soc.*, **1954**, 1226, 2189; *J. Am. Chem. Soc.*, **75**, 5930, 5932 (1953) and literatures cited there.

3) H. Bruderer, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **39**, 858 (1956) and literatures cited there.

4) a) J. Lecomte and C. Dufour, *Compt. rend.*, **234**, 1887 (1952); b) J. Lecomte and H. Gault, ibid., **238**, 2538 (1954).

5) S. Lieberman and D. K. Fukushima, *J. Am. Chem. Soc.*, **72**, 5211 (1950).

* Cf. M. A. Romero, *J. Org. Chem.*, **22**, 1267 (1957).

TABLE I

SYNTHESIS OF TESTOSTERONE FROM A MIXTURE OF 4-ANDROSTENE-3α,17β- AND -3β,17β-DIOLS BY TREATMENT WITH ACTIVE *N*-HALOGEN COMPOUNDS

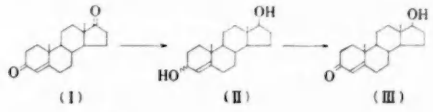
No.	androstenediol (mg.)	*N*-hlogene compounds (mg.) (equiv.)	solvents (ml.)	conditions (°C) (hr.)	yields of testosterone (wt.%)
1	147.6	NBA, (76.2) (1.09)	Bu, 10; Py, 0.5; W, 0.3	20~21, 17	45
2	151.1	NBA, (77.1) (1.07)	Bu, 10; Py, 1; W, 1	15~17, 19	52
3	151.4	NBA, (77.5) (1.08)	Bu, 1; Py, 0.5	20~21, 17	71
4	152.0	NBA, (78.6) (1.09)	Bu, 0.5; Py, 1	20~21, 17	69
5	152.8	NBA, (75.9) (1.05)	Bu, 10; Py, 1	15~17, 19	68
6	151.5	NBA, (79.5) (1.10)	Bz, 2; Py, 1	20~21, 17	74
7	152.9	NBA, (76.4) (1.05)	Bz, 3; Py, 0.5	16~18, 41	57
8	151.9	NBA, (75.9) (1.05)	Bz, 8; Py, 0.1	16~18, 23	45
9	151.1	NBA, (76.0) (1.06)	Chf, 2; Py, 1	20~21, 17	47
10	152.6	NBA, (74.0) (1.02)	E, 4; Me, 10; Py, 0.3; W, 0.3	15~17, 19	38
11	152.2	NBS, (97.1) (1.03)	Bu, 0.5; Py, 1	15~17, 19	56
12	148.3	NBS, (100.1) (1.1)	E, 4; Me, 10; Py, 0.3; W, 0.3	15~17, 19	39
13	250.7*	NBS, (163.0) (1.06)	E, 5; Me, 1; 3%$KHCO_3$aq., 0.3	29 18	33
14	151.0	62% ICB, (116.8) (1.14)	Bz, 5; Py, 2	49~51, 1	71
15	155.5	62% ICB, (103.0) (0.98)	Bz, 10; Py, 0.3	50~52, 1	55
16	149.4	72% ICB, (91.3) (1.05)	Bu, 2; Py, 2	60~63, 1	73
17	175.6*	83% ICB, (98.6) (1.1)	Bu, 2; Py, 0.3; W, 0.3	60~65, 1	64

Bu=*tert*-Butanol, Py=Pyridine, W=Water, Bz=Benzene, Chf=Chloroform, E=Ether, Me=Methanol, NBA=*N*-Bromoacetamide, NBS=*N*-Bromosuccinimide, ICB=Isocyanur bromide.

* Eight grams of alumina were used.

reagents for selective oxidation of allylic alcohols.

The reduction of 4-androstene-3, 17-dione (I) with sodium borohydride gave a mixture of 4-androstene-3α, 17β-diol and the corresponding 3β, 17β-diol. The mixture, m.p. 95~145°C[6], was oxidized with about 1.05 equivalents of *N*-bromoacetamide, *N*-bromosuccinimide or isocyanur bromide[10] in various solvents, and the products were separated by chromatography. The results are shown in Table I. It is clear that (1) water disturbs* this reaction especially when used with *N*-bromosuccinimide or *N*-bromoacetamide, (2) *N*-bromoacetamide and isocyanur bromide are superior to *N*-bromosuccinimide as the reagents of this reaction. In the best conditions testosterone (III) was obtained in 70~74% overall yield from 4-androstene-3, 17-dione (I). (No. 3, 4, 6, 14 and 16)



(I) (II) (III)

Progesterone (IV) was reduced with sodium borohydride to give a mixture of 4-pregnene-3α, 20β-diol and the corresponding 3β, 20β-diol. The mixture, m. p. 147~168°C[11], was oxidized with *N*-bromoacetamide in benzene-pyridine. 4-Pregnen-20β-ol-3-one (VI) was obtained in

6) Sondheimer et al.[7] reported that the reduction of compound I with lithium aluminum hydride furnished a mixture of the 3α, 17β-diol and the 3β, 17β-diol and the mixture melted at 165~171°C. Presumably the difference in the melting points of both mixtures is due to difference in the proportions of 3α and 3β alcohols[8], since the C_{17} carbonyl group was exclusively reduced to the β-hydroxyl group on reduction with sodium borohydride[9].

7) F. Sondheimer, C. Amendolla and G. Rosenkranz, *J. Am. Chem. Soc.*, **75**, 5930 (1953).

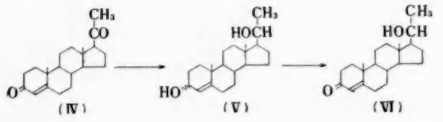
8) For sodium borohydride reduction of 4-ene-3-ketosteroids see, W. W. Zorbach, ibid., **75**, 6344 (1953); B. Camerino and C. G. Alberti, *Gazz. chim. ital.*, **85**, 51 (1955); S. Bernstein, S. M. Stolar and M. Heller, *J. Org. Chem.*, **22**, 472 (1957).

9) H. J. Ringold, B. Loeken, G. Rosenkranz and F. Sondheimer, *J. Am. Chem. Soc.*, **78**, 816 (1956); K. Miescher and C. Meystre, U. S. Pat. 2,679,502; *Chem. Abst.*, **49**, 6325^i (1955).

10) K. Morita, This Bulletin, **31**, 347 (1958).

11) Reduction of progesterone with lithium aluminum hydride gives a mixture with m. p. 162~172°C[7].

76% overall yield from progesterone (IV). The 20β configuration was deduced from α_D values of compound VI, +85°, and of its acetate, +130°, which were quite similar to the reported[7,12-14]. Sondheimer et al.[7] reported that the reduction of progesterone (IV) with lithium aluminum



hydride and the succeeding oxidation of the resulted diols with manganese dioxide yielded compound VI in 66% overall yield.

Manganese dioxide attacks preferably unhindered hydroxyl groups such as primary[3] or equatorial hydroxyl[15]. On the other hand, active *N*-halogen compounds attack rather hindered hydroxyl groups[16,17]. The rate-determining step of the latter reaction is known to be the abstraction of the hydrogen atom bonded to the carbinol carbon. *N*-Halogen compounds might be serviceable for selective oxidation of polyhydroxyl compounds carrying primary or equatorial and allylic hydroxyl groups to α, β-unsaturated ketones with unaffected primary or equatorial hydroxyl groups. Such selective oxidation is probably difficult[3] when manganese dioxide is employed. Examples will be reported soon.

Experimental[18]

General Procedure of Synthesis of Testosterone (III) from 4-Androstene-3,17-dione (I).—A mixture of 1 g. of 4-Androstene-3,17-dione (I) with m.p. 165~169°C in 10 ml. of methanol and 1 g. of sodium borohydride in 1 ml. of water was heated under reflux for 1 hour. After cooling, the suspension was poured into dilute hydrochloric acid. Solid was collected by filtration and well washed with water. It melted at 95~145°C, and was presumably essentially a mixture of 4-androstene-3α, 17β- and 3β, 17β-diols and gave no 2, 4-dinitrophenylhydrazone.

A weighed sample from the above solid in a mixed solvent as described in Table I was treated with *N*-bromoacetamide, *N*-bromosuccinimide or isocyanur bromide in the dark. When a solid appeared, it was filtered off. The solution or filtrate was diluted with a mixture of 30 ml. of ether and 10 ml. of benzene and washed successively with 10% aqueous sodium bisulfite, with 10% aqueous sodium hydroxide, with water, with dilute sulfuric acid and again with water, and dried over anhydrous sodium sulfate. The solvent was evaporated under a reduced pressure. The oily or crystalline residue was dissolved in 10 ml. of benzene and adsorbed on a column of alumina (5 g.).

The elution of products was carried out with the following solvent systems[19].

Fraction No.	benzene (ml.)	ether (ml.)
1	12	2
2	14	4
3	6	4
	4	6
4	6	14
5	4	16
6	2	18
7	0	20
	aceton (ml.)	ether (ml.)
8	2	18
9	4	16
10	6	14
11	8	12
12	methanol 30 ml.	

The earlier fractions gave 4-androstene-3, 17-dione (I) or an oil. The dione, collected from all the experiments and recrystallized from acetone-*n*-hexane, exhibited m. p. 168~169°C, λ_{max} 240mμ, log ε 4.23. Identity was established by a mixed melting point determination.

From middle fractions testosterone (III) with m. p. 148~153°C and mixed m. p. above 149°C was obtained in yields shown in Table I. Testosterone from all the experiments was brought together and recrystallized from acetone-*n*-hexane to show m. p. 152~153°C; $[\alpha]_D^{19}$ +102 (c, 1.40 in dioxan); λ_{max} 241 mμ, log ε 4.21.

From later fractions the starting material or an oil was obtained. Some oily fractions showed positive Beilstein test. Such oily fractions increased when water and/or *N*-bromosuccinimide was used.

4-Pregnene-20β-ol-3-one (VI) from Progesterone(IV).—A mixture of 1.5 g. of progesterone with m. p. 125~127°C in 30 ml. of methanol and 1 g. of sodium borohydride in 1.5 ml. of water was heated under reflux for one hour. After

12) P. Wieland and K. Miescher, *Helv. Chim. Acta*, **32**, 1922 (1949).
13) J. Romo, M. Romo, C. Djerassi and G. Rosenkranz, *J. Am. Chem. Soc.*, **73**, 1528 (1951).
14) R. B. Turner and D. M. Voitle, ibid., **73**, 2283 (1951).
15) C. Amendolla, G. Rosenkranz and F. Sondheimer, *J. Chem. Soc.*, **1954**, 1256; also see footnote 16 of Ref. 3.
16) The oxidation of primary alcohols with *N*-bromoacetamide is difficult. Cf. R. E. Jones and F. W. Kocher, *J. Am. Chem. Soc.*, **76**, 3682 (1954); T. H. Krichevsky, D. L. Garmaise and T. F. G. Gallagher, ibid., **74**, 483 (1952).
17) Axial hydroxyl groups are more easily oxidized to carbonyl than equatorial ones. Cf. W. Klyne, "Progress in Stereochemistry" **1**, Butterworths Scientific Publications, London (1954), p. 63.
18) All melting points are uncorrected. Ultraviolet absorption spectra were measured in 95% ethanol solution with a Hitachi Photoelectric Spectrophotometer Model EPU-2.
19) The chromatographic separations were carried out in part by Mr. T. Iwama to whom author's thanks are due.

cooling a few drops of acetic acid were added and the solution was poured into an excess of water. The solid was collected by filtration and well washed with water. The mixture of 4-pregnene-3α,20β- and 3β,20β-diols melted at 147~168°C. Yield 1.5 g.

A solution of 499.1 mg. of above solid in 3 ml. of benzene and 5 ml. of pyridine was treated with 265.7 mg. of *N*-bromoacetamide (1.22 equiv.) at 18~19°C for two hours. After treated as usual, the crystalline residue was dissolved in 15 ml. of benzene and adsorbed on a column of alumina (3 g.). The elution with benzene-ether (1 : 1) and recrystallization from ether-*n*-hexean gave needles with m. p. 169~171°C, $[\alpha]_D^{19}$+85 (c, 1.05 in chloroform), λ_{max}242 mμ, log ε 4.22. Yield 378 mg. or 76 % of the theoretical. Identity was established by a mixed[7] melting point determination. Reported m. p. 171~172°C, $[\alpha]_D$+84[12]; m. p. 169~171°C, $[\alpha]_D$+83, λ_{max}242 mμ, log ε 4.31[13]; m. p. 174~175°C, $[\alpha]_D$+90[14]; m. p. 174~175°C, $[\alpha]_{\cdot\cdot}$+86, λ_{max}240 mμ, log ε 4.23[7].

The acetate, recrystallized from acetone-*n*-hexane, exhibited m. p. 159~160°C, $[\alpha]_D^{18}$+130 (*c*, 0.368 in chloroform). Reported m. p. 159~160°C, $[\alpha]_D$+140[12], m. p. 159~161°C, $[\alpha]_D$+137[13], m. p. 161~162°C, $[\alpha]_D$+129[14], m. p. 161~162°C, $[\alpha]_D$+134[7].

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Electronic Structure and Spectra of s-Tetrazine

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Recently, we have studied the electronic structure and the spectra of some nitrogen heterocycles using a semiempirical LCAO SCF MO method[1]. Our investigation has given a theoretical ground to the classification of the spectra of nitrogen heterocycles which has been made by Zanker[2] in analogy to the spectra of aromatic hydrocarbons. The cause of the intensification of ^1L_b band in a nitrogen heterocycle compared with the corresponding aromatic hydrocarbon, was ascribed by some authors[3,4], for example, in the case of pyridine and benzene, to the mixing of unperturbed $^1B_{2u}$ state to which transition from the ground state is virtually forbidden, with some contribution from $^1E_{1u}$ state to which transition is strongly allowed. Tsubomura[5] has studied the same problem, using an antisymmetrized product of naive MO. He has examined the above described possibility and also another possibility that, in pyridine, the lowering of molecular symmetry compared with benzene, may cause the perturbation on MO in the direction of C_{2v} axis, and this perturbation may also lead to the intensification of ^1L_b band. His conclusion is, however, that the latter effect may be small compared with the former. We have confirmed[1] that the latter effect is negligibly small compared with the former, on the basis of SCF MO. In the present paper, we shall report the results obtained for *s*-tetrazine, a typical nitrogen heterocycle, comparing them with the results for some nitrogen heterobenzenes such as pyridine and pyrazine, and discuss the nature of electonic transition in the *s*-tetrazine molecule.

Theoretical Method[1]

The present section is devoted to a brief description of the main ideas and approximations in the theory.

A) Formulation. — The theoretical method is based on the framework of the LCAO SCF MO method developed by

1) N. Mataga and K. Nishimoto, *Z. physik. Chem., N. F.*, **13**, 140 (1957).
2) V. Zanker, ibid., **2**, 52 (1954).
3) W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954).
4) N. Mataga et al., This Bulletin, **29**, 373 (1956).
5) H. Tsubomura, *J. Chem. Soc. Japan, Pure. Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 293 (1957).

Roothaan[6] and Hall[7], with only the π-electrons considered explicitly. Its computation procedure is similar to that of Pople[8] and Ooshika[9]. The wave function for the π-electron in the ground state was taken as a Slater determinant built up from orthonormal moleculer orbitals which are themselves linear combinations of $2p\pi$ atomic orbitals $\phi_1 \cdots\cdots \phi_{2m}$ of carbon or nitrogen,

$$\psi_i = \sum_\mu c_{i\mu}\phi_\mu \tag{1}$$

The coefficients $c_{i\mu}$ are chosen to minimize the electronic energy,

$$E = \int \chi_0 \mathbf{H} \chi_0 d\tau \tag{2}$$

where $\mathbf{H}$ is the complete electronic Hamiltonian

$$\mathbf{H} = \sum_i H_i^{core} + \sum_{i<j}^{2m} (e^2/_{ij}) \tag{3}$$

The general set of equations for $c_{i\mu}$ which has been given by Roothaan[6] can be reduced to the following eigenvalue equations, by some simplifying approximations about the integrals that arise[8-10].

$$\sum_\nu F_{\mu\nu} c_{i\nu} = \varepsilon_i c_{i\mu} \tag{4}$$

where

$$F_{\mu\mu} = H_{\mu\mu} + \frac{1}{2} P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\kappa(\neq\mu)} P_{\kappa\kappa}\gamma_{\kappa\mu} \tag{5}$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu}\gamma_{\mu\nu} \tag{6}$$

$$P_{\mu\nu} = 2\sum_{j=1}^{m} c_{j\mu} c_{j\nu} \tag{7}$$

$\gamma_{\mu\nu}$ is the interelectronic Coulomb repulsion integral

$$\gamma_{\mu\nu} = \int \phi_\mu^*(1)\phi_\nu^*(2) \frac{e^2}{r_{12}} \phi_\mu(1)\phi_\nu(2) d\nu_1 d\nu_2 \tag{8}$$

$H_{\mu\mu}$ are the diagonal matrix elements of the core Hamiltonian for all atoms,

$$\begin{aligned} H_{\mu\mu} &= \int \phi_\mu^* \left\{ -\frac{1}{2}\nabla^2 - \sum_\kappa V_\kappa \right\} \phi_\mu d\nu \\ &= \int \phi_\mu^* \left\{ -\frac{1}{2}\nabla^2 - V_\mu \right\} \phi_\mu d\nu \\ &\quad - \sum_{\kappa(\neq\mu)} \int \phi_\mu^* V_\kappa \phi_\mu d\nu \\ &= \alpha_\mu - \sum_{\kappa(\neq\mu)} \gamma_{\kappa\mu}' \end{aligned} \tag{9}$$

where

$$\alpha_\mu = \int \phi_\mu^* \left\{ -\frac{1}{2}\nabla^2 - V_\mu \right\} \phi_\mu d\nu \tag{10}$$

$$\gamma_{\kappa\mu}' = \int \phi_\mu^* V_\kappa \phi_\mu d\nu \tag{11}$$

α_μ may be regarded as a quantity characteristic to μ atom in an appropriate valence state and for our purpose, it may be satisfactory to assume, $\gamma_{\kappa\mu}' = \gamma_{\kappa\mu}$[8].

We denote $H_{\mu\nu}$, the off-diagonal matrix elements of the core Homiltonian, as $\beta_{\mu\nu}$,

$$\beta_{\mu\nu} = \int \phi_\mu^* \left\{ -\frac{1}{2}\nabla^2 - \sum_\kappa V_\kappa \right\} \phi_\nu d\nu \gamma_{\kappa\mu} \tag{12}$$

then the matrix elements of the ground state Fock Hamiltonian may be written as follows, using the approximations described above,

$$F_{\mu\mu} = \alpha_\mu + 1/2 P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\kappa(\neq\mu)} (P_{\kappa\kappa} - 1) \tag{13}$$

$$F_{\mu\nu} = \beta_{\mu\nu} - 1/2 P_{\mu\nu}\gamma_{\mu\nu} \tag{14}$$

When the self-consistent problem for the ground state has been solved by a cyclic process, the unoccupied orbitals $\phi_{m+1} \cdots\cdots \phi_{2m}$ can be used to construct configurational wave functions for excited states. We shall write ${}^1\chi_{i\to k}$ for the singlet configurational wave function in which one electron is excited from an occupied orbital ϕ_i to an unoccupied orbital ϕ_k. The corresponding triplet wave function will be written ${}^3\chi_{i\to k}$, and $({}^1\chi_{i\to k}|\mathbf{H}|{}^1\chi_{j\to l})$ and $({}^3\chi_{i\to k}|\mathbf{H}|{}^3\chi_{j\to})$ represent the matrix elements of total Hamilton $\mathbf{H}$ by these wave functions. Then the excitation energies corresponding to the transition $i\to k$ are expressed as follows for singlet and triplet respectively :

$$\begin{aligned} E({}^1\chi_{i\to k}) &= ({}^1\chi_{i\to k}|\mathbf{H}|{}^1\chi_{i\to k}) - (\chi_0|\mathbf{H}|\chi_0) \\ &= \varepsilon_k - \varepsilon_i - (ik|G|ik) + 2(ik|G|ki) \end{aligned} \tag{15}$$

$$\begin{aligned} E({}^3\chi_{i\to k}) &= ({}^3\chi_{i\to k}|\mathbf{H}|{}^3\chi_{i\to k}) - (\chi_0|\mathbf{H}|\chi_0) \\ &= \varepsilon_k - \varepsilon_i - (ik|G|ik) \end{aligned} \tag{16}$$

where

$$(pq|G|rs) = \int \psi_p^*(1)\psi_q^*(2) \frac{e^2}{r_{12}} \psi_r(1)\psi_s(2) d\nu_1 d\nu_2 \tag{17}$$

The interconfigurational matrix elements may be written in a similar way

$$({}^1\chi_{i\to k}|\mathbf{H}|{}^1\chi_{i\to k}) = 2(jk|G|li) - (jk|G|il) \tag{18}$$

$$({}^3\chi_{i\to k}|\mathbf{H}|{}^3\chi_{i\to k}) = -(jk|G|il) \tag{19}$$

An excited state wave function Ψ_a is approximated by a linear combination of singly excited configuration functions $\chi_{i\to k}$'s.

6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 61 (1951).
7) G. G. Hall, *Proc. Roy. Soc.*, **A205**, 541 (1951).
8) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).
9) Y. Ooshika, *J. Phys. Soc. Japan*, **12**, 1238 (1957)
10) J. A. Pople, *Trans. Faraday. Soc.*, **49**, 1357 (1953).

The oscillator strength, f, is calculated by the method described by Mulliken and Rieke,

$$f=1.085\times10^{11}\omega_{0\alpha}\sum_{r=x,y,z}[Q_{0\alpha}r]^2 \qquad (20)$$

where $\omega_{0\alpha}$ is the frequency of the $\chi_0\rightarrow\Psi_\alpha$ transition in cm^{-1}.

B) Semiempirical Evaluation of Integrals.—Molecular integrals appeared in Eqs. 13 and 16 are evaluated by semiempirical procedure analogous to, but somewhat different from those given by Pariser and Parr[11], Ooshika[9] and Pople[10].

B1. The value of α_μ was taken to be equal to $-I_\mu$, where I_μ is the ionization potential of μ atom in the appropriate atomic valence state[12]. $\beta_{\mu\nu}$ for C–N and N–N were taken from Pariser and Parr[11] and Paoloni[13], respectively, for nearest neighbours and neglected for more distant neighbors:

$$\beta_{CN}=-2.576\ e.v.,\quad \beta_{NN}=-2.35\ e.v.*$$

B2. To estimate the two center Coulomb repulsion integrals of the type $\gamma_{\mu\nu}$, we used the following approximation,

$$\gamma_{\mu\nu}=e^2/R_{\mu\nu} \qquad (21)$$

$$R_{\mu\nu}=a+r_{\mu\nu} \qquad (22)$$

where $r_{\mu\nu}$ is the interatomic distance between μ and ν atoms. a is a parameter, which is determined in the following way, using valence state ionization potential I_μ and electron affinity A_μ in the same valence state. For homonuclear two centers, we put

$$\gamma_{\mu\mu}=e^2/R_{\mu\mu}=e^2/a=I_\mu-A_\mu \qquad (23)$$

In the case of heteronuclear two centers, i.e. carbon and nitrogen, we take as $e^2/R_{\mu\mu}$, simple arithmetic mean of $e^2/R_{\mu\mu}$'s for carbon and nitrogen. The values of a thus evaluted are, $a_{CC}=1.328$Å, $a_{CN}=1.212$Å and $a_{NN}=1.115$ Å. The geometrical structure of *s*-tetrazine has been determined by Bertinotti, Giacomello and Liquori[14], by means of X-ray diffraction. The values of $r_{\mu\nu}$'s necessary for the evaluation of $\gamma_{\mu\nu}$'s and oscillator strength were taken from this work.

Results and Discussion

As pointed out previously[1], the replacement of —CH= with —N= can be regarded as a small perturbation, and the SCF MO's of nitrogen hetrocycles are nearly close to the naive MO's obtained by ordinary procedure, assuming the Coulomb integral at nitrogen atom, α_N, to be equal to $\alpha+0.5\beta$.

We have chosen the naive MO's of *s*-tetrazine obtained in this way as a starting MO's for the SCF calculation. Thus the self-consistent problem for *s*-tetrazine has been solved and the resulting SCF MO's and MO energies are collected in Table I.

TABLE I
SCF MO'S AND MO ENERGIES OF *s*-TETRAZINE

Symmetry	ε_i(*e.v.*)	
b_{2u}	−15.531	$\psi_1=0.4277\sigma_1+0.3667\sigma_2$
b_{1g}	−12.759	$\psi_2=0.5000\sigma_3$
b_{3g}	−11.973	$\psi_3=0.3256\sigma_4+0.5365\sigma_5$
a_{1u}	− 2.899	$\psi_4=0.5000\sigma_6$
b_{2u}	− 1.573	$\psi_5=0.2592\sigma_1-0.6046\sigma_2$
b_{3g}	0.975	$\psi_6=0.4374\sigma_4-0.3424\sigma_5$

$\sigma_1=(\phi_2+\phi_3+\phi_5-\phi_6)$, $\sigma_3=(\phi_1+\phi_4)$, $\sigma_5=(\phi_2+\phi_3-\phi_5-\phi_6)$

$\sigma_2=(\phi_2-\phi_3-\phi_5+\phi_6)$, $\sigma_4=(\phi_1-\phi_4)$, $\sigma_6=(\phi_2-\phi_3+\phi_5-\phi_6)$

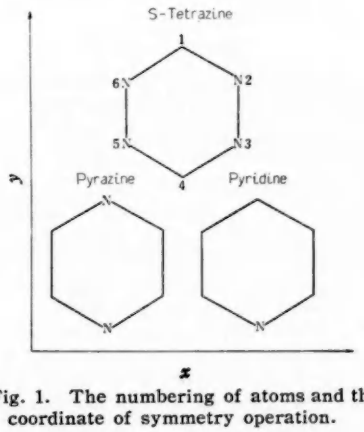

Fig. 1. The numbering of atoms and the coordinate of symmetry operation.

11) R. Pariser and R. G. Parr, (a) *J. Chem. Phys.*, **21**, 466 (1953); (b) ibid., **21**, 767 (1953); (c) ibid., **23**, 711 (1955); (d) R. Pariser, ibid., **24**, 250 (1956).

12) The values of ionization potentials and electron affinities in the valence state are taken from: H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

13) L. Paoloni, *J. Chem. Phys.*, **25**, 1277 (1956).

*) Note added in proof: Paoloni has used the ASMOCI method. Although he has employed the value −2.34 e.v. in ref. 13), he has pointed out in another place§ that β_{NN} could be as low as −1 e.v. if one invokes the configuration interaction among χ_0, $\chi_{2\rightarrow6}$ and $\chi_{1\rightarrow4}$. However, in our present theory which takes into consideration only a limited amount of configuration interaction, the best choise of β_{NN} value seems to be the one employed here. The author is grateful to Dr. L. Paoloni of Rome University for illuminating discussions on this point.

§ L. Paoloni, Gazz. chim. ital., **87**, 313 (1957).

14) F. Bertinotti, G. Giacomello and A. M. Liquori, *Acta Cryst.*, **8**, 513 (1955); ibid., **9**, 510 (1956).

TABLE II
THE ENERGIES OF CONFIGURATIONS AND THE VALUES OF INTERCONFIGURATIONAL MATRIX ELEMENTS*

$\Psi(^1B_{3u}^-) = 0.8691\,{}^1\chi_{3\to4} - 0.4945\,{}^1\chi_{2\to5}$ $E(^1\chi_{3\to4}) = 5.7479$
$\Psi(^1B_{3u}^+) = 0.4945\,{}^1\chi_{3\to4} + 0.8691\,{}^1\chi_{2\to5}$ $E(^1\chi_{2\to5}) = 7.2810$
$(^1\chi_{3\to4} \mid \mathbf{H} \mid {}^1\chi_{2\to5}) = 1.2901$
$\Psi(^3B_{3u}^-) = 0.2181\,{}^3\chi_{3\to4} - 0.9759\,{}^3\chi_{2\to5}$ $E(^3\chi_{3\to4}) = 3.4231$
$\Psi(^3B_{3u}^+) = 0.9759\,{}^3\chi_{3\to4} + 0.2181\,{}^3\chi_{2\to5}$ $E(^3\chi_{2\to5}) = 5.8077$
$(^3\chi_{3\to4} \mid \mathbf{H} \mid {}^3\chi_{2\to5}) = -0.5607$
$(34 \mid G \mid 34) = 5.6509$, $(34 \mid G \mid 43) = 1.1624$,
$(25 \mid G \mid 25) = 5.3782$, $(25 \mid G \mid 52) = 0.7366$
$\Psi(^1B_{1u}^-) = 0.0927\,{}^1\chi_{2\to4} - 0.9957\,{}^1\chi_{3\to5}$ $E(^1\chi_{2\to4}) = 6.8708$
$\Psi(^1B_{1u}^+) = 0.9957\,{}^1\chi_{2\to4} + 0.0927\,{}^1\chi_{3\to5}$ $E(^1\chi_{3\to5}) = 9.9633$
$(^1\chi_{2\to4} \mid \mathbf{H} \mid {}^1\chi_{3\to5}) = -0.2899$
$\Psi(^3B_{1u}^-) = 0.1598\,{}^3\chi_{2\to4} - 0.9871\,{}^3\chi_{3\to5}$ $E(^3\chi_{2\to4}) = 3.1924$
$\Psi(^3B_{1u}^+) = 0.9871\,{}^3\chi_{2\to4} + 0.1598\,{}^3\chi_{3\to5}$ $E(^3\chi_{3\to5}) = 6.5663$
$(^3\chi_{2\to4} \mid \mathbf{H} \mid {}^3\chi_{3\to5}) = -0.5607$
$(24 \mid G \mid 24) = 6.6683$, $(24 \mid G \mid 42) = 1.8392$,
$(35 \mid G \mid 35) = 3.8329$, $(35 \mid G \mid 53) = 1.6985$

* The energies are in unit of *e. v.*

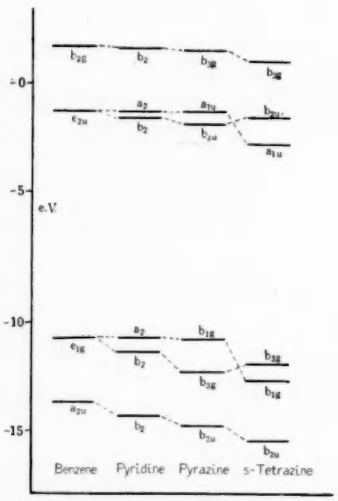

Fig. 2. SCFMO energies of benzene, pyridine, pyrazine and *s*-tetrazine.

The numbering of atoms and the coordinate for the symmetry operation are shown in Fig. 1. For the purpose of comparison, the SCF MO energies are indicated in Fig. 2 together with those of benzene, pyridine and pyrazine[1].

It is evident from Fig. 2 that both of the doubly degenerate benzene MO's e_{1g} and e_{2u} are split into two MO's with different energies in pyridine, pyrazine and *s*-tetrazine owing to the lowering of molecular symmetry. In pyrazine, b_{1g} is higher than b_{3g} in the occupied MO's, and in the vacant MO's a_{1u} is higher than b_{2u}. When molecular symmetry is reduced from D_{2h} in pyrazine to C_{2v} in pyridine, a_{1u} and b_{1g} become a_2, and b_{2u} together with b_{3g} become b_2. In addition, the former is higher than the latter, in the case of pyridine, both in the occupied and the vacant MO's. In the case of *s*-tetrazine, the relative order of the coresponding levels is reversed. The cause of this reversal may plausibly be attributed to the strengthening of the core potential, resulting from the increase of the number of nitrogen atoms. The excited state wave functions, energies of configarations and the values of interconfigurational matrix elements are given in Table II.

The calculated excitation energies and oscillator strengths are collected in Table III, in comparison with the observed values. Unfortunately, the experimental

TABLE III
EXCITATION ENERGIES AND OSCILLATOR STRENGTHS

Symmetry		Excitation energy (*e.v.*)		Oscillator strength	
Group theory	Platt	calc.	obs.	calc.	obs.
$^1B_{3u}^-$	^1L_b	5.013	4.96[a]	0.11	—
$^1B_{1u}^+$	^1L_a	6.842	—	0.43	—
$^1B_{3u}^+$	^1B_b	8.015	—	1.35	—
$^1B_{1u}^-$	^3L_a	9.990	—	0.73	—
$^3B_{1u}^+$	^3L_a	3.101	—	0	—
$^3B_{3u}^+$	^3B_b	3.298	—	0	—
$^3B_{3u}^-$	^3L_b	5.933	—	0	—
$^3B_{1u}^-$	^3B_a	6.657	—	0	—

a) Ref. 15)

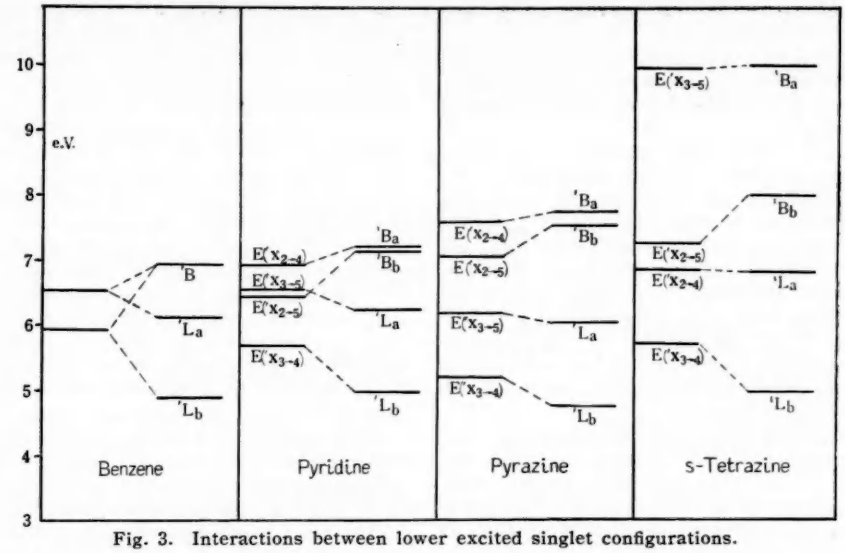

Fig. 3. Interactions between lower excited singlet configurations.

data are not sufficient, and only the value of excitation energy for the lowest singlet $\pi\to\pi$ transition is available[15]. For this transition, the calculated excitation energy agrees satisfactorily with the observed one.

The configuration integration between the singlet excited configurations are illustrated in Fig. 3 together with results[1] for benzene, pyridine, for the purpose of comparison. It is clear, from the results given in Fig. 3, that the configuration interaction plays a very important role for the determination of the spectra. Let us consider, for example, the case of the lowest singlet excited state, $^1B_{3u}$. The two configurations, $^1\chi_{3\to4}$ and $^1\chi_{2\to5}$ are degenerate in benzene, and the degree of splitting due to configuration interaction is very large. The two configurations are no longer degenerate in pyridine, *s*-tetrazine and pyrazine, and the energy difference between the two configurations becomes larger in this order. The magnitude of the splitting is, however, the smaller, the larger is the energy difference between the two configurations. Thus the relative hight of $^1B^-{}_{3u}$ state in this series of nitrogen heterocycles is approximately unchanged, and almost the same as that in benzene. This circumstance of the configuration interaction in nitrogen heterocycles has already been discussed qulitatively by Tsubomura[5], and his conclusion is confirmed by our quantitative study described above. It may be a very interesting problem whether such an argument is still applicable to the electronic spectra of pyridinium ion, the lowest excited state of which has almost the same excitation energy as that of pyridine*.

As mentioned above, we have pointed out previously[1], that the perturbation on MO by hetro-replacement may have only small influence on the oscillator strength, and almost all the part of the latter may arise from the inequality of a and b in Eq. 24.

$$\Psi(\Gamma)=a\chi_1+b\chi_2 \qquad (24)$$

where $\Psi(\Gamma)$ is an excited-state wave function and χ_1 and χ_2 are two configurations interacting upon each other.

That the same circumstance prevails also in the case of *s*-tetrazine is evident from the following analysis. Let us put $a=b$ in Eq. 24, then the oscillator strengths of *s*-tetrazine become as follows.

Γ	f
$^1B^-{}_{3u}$	0.01
$^1B^+{}_{1u}$	0.008

In fact, these values of f are very small compared with the actual values of

15) A. M. Liquori and A. Vaciago, *Ric. Scient.*, **26**, 181 (1956); *Gazz. chim. ital.*, **86**, 759 (1956).

* In this respect, the present author, in collaboration with Miss S. Tsuno, is now working out the electronic structure of pyridinium ion.

calculated oscillator strength and are almost negligible.

Now let us refer to the polarizations of transitions in this molecule, though there are no such experimental data available at present.

With the results and reasonings described hitherto, the polarization of transition to the lowest excited state may be polarized in x direction of Fig. 1, where, in addition to *s*-tetrazine, pyridine and pyrazine are pictured for the convenience of comparison, their corresponding transitions being polarized also in x direction of the figure. The transition to the second excited state, however, is polarized in y direction in *s*-tetrazine as well as in pyridine and pyrazine.

Eventually, the spectral similarity of *s*-tetrazine with the parent hydrocarbon and the other nitrogen heterocycles such as pyridine and pyrazine originates from the close correspondence of the MO's of the former with those of the latter, though the MO energies of *s*-tetrazine are considerably different from those of the others. Whereas the relative order of b_{1g} and b_{3g} or a_{1u} and b_{2u} orbitals in energy scale is reversed in *s*-tetration compared with those in pyrazine or pyridine, the result of configuration interaction gives the excitation energy of the transition to the lowest excited state which is almost the same as those of pyrazine, pyridine and benzene, in good agreement with the experimental observation.

Summary

(1) π-Electronic structure and the nature of the electronic transitions in the *s*-tetrazine molecule has been elucidated using the semiempirical LCAO SCF MO method.

(2) There is satisfactory agreement between the calculated and the observed values of the excitation energy for the transition to the lowest excited state.

(3) Tsubomura's qualitive argument concerning the influence of configuration interaction on the lowest energy transition of nitrogen heterocycles has been confirmed by the quantitative calculation.

(4) The cause of the intensification of ^1L_b band compared with the parent hydrocarbon has been analysed by the same method employed previously[1], and it has been confirmed that, also in the case of *s*-tetrazine the perturbation on MO by hetero-replacement has only a small influence on the oscillator strength.

(5) The spectral simirarity of nitrogen heterocycles with the parent hydrocarbon has been ascribed to the fact that their MO's correspond closely each other, and it has been pointed out that the configuration interaction plays a very important role in the determination of spectra, which is also a cause for the spectral similarity.

The autor expresses his gratitude to Professor S. Mizushima of Tokyo University for his encouragement. He also expresses his cordial thanks to Professor R. Fujishiro for his interest and encouragement during the present study. He is grateful to Dr. S. Nagakura of Tokyo University and Dr. H. Tsubomura of Tokyo University for their illuminating discussions. He also express his hearty thanks to Mr. K. Nishimoto and Miss S. Tsuno for their helpful discussions.

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Electronic Spectra of Quinoline and Isoquinoline and the Mechanism of Fluorescence Quenching in These Molecules

By Noboru MATAGA

(Received December 18, 1957)

In the previous papers[1,2] we have reported detailed theoretical studies on the electronic structure and the nature of electronic transitions of some nitrogen heterocycles, using the semiempirical SCF method. The detailed Hartree-Fock SCF study has been made only for nitrogen heterobenzenes, and some semiquantitative extentions to larger molecules such as acridine and phenazine have been made on the basis of the results obtained for nitrogen heterobenzenes. Even by the latter very approximate method, the general feature of the electronic spectra is fairly well comprehended. In the present report and also in following one, we shall employ a more rigorous method and give a more detailed interpretation and reasoning on the nature of the electronic transitions in some two and three ring-nitrogen heterocycles such as quinoline, isoquinoline, acridine and phenazine.

Method

The Hartree-Fock self-consistent field method applied to molecules in terms of MO's, determines the best MO's for approximate ground state, and these MO's may also be satisfactory in describing the excited states[3]. As pointed out by McWeeny[4], however, it may be possible that other choices of MO's may give a comparable result for the interpretation of electronic spectra. From such a viewpoint, rather than pursuing a laborious iterative calculation of SCF, we have assumed that SCF MO's of the parent hydrocarbon[5], naphthalene, may be a satisfactory approximation to the MO's of quinoline and isoquinoline for the description of the excited states. Then the orbital energy of the i-th orbital, ε_i, and the excitation energy of the $i\rightarrow k$ transition, $E(\chi_{i\rightarrow k})$ may be calculated by the following equation[1,2].

$$\varepsilon_i=\int\phi_i^* F\phi_i d\upsilon=\sum_{\mu,\nu} c^*_{i\mu}c_{i\nu}F_{\mu\nu} \tag{1}$$

where F is the Fock's Hamiltonian and ϕ_i is the LCAO MO of the parent hydrocarbon,

$$\phi_i=\sum_{\mu} c_{i\mu}\phi_\mu \tag{2}$$

$$F_{\mu\mu}=\alpha_\mu+\frac{1}{2}P_{\mu\mu}\gamma_{\mu\mu}+\sum_{\kappa(\neq\mu)}(P_{\kappa\kappa}-1)\gamma_{\mu\kappa} \tag{3}$$

$$F_{\mu\nu}=\beta_{\mu\nu}-\frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \tag{4}$$

The last term in the right hand side of Eq. 3 vanishes because of the uniform charge density, $P_{\kappa\kappa}=1$, in the parent hydrocarbon.

$$F_{\mu\mu}=\alpha_\mu+\frac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} \tag{3'}$$

$$E(^1\chi_{i\rightarrow k})=\varepsilon_k-\varepsilon_i-(ik\,|\,G\,|\,ik)+2(ik\,|\,G\,|\,ki), \tag{5}$$

$$E(^3\chi_{i\rightarrow k})=E(^1\chi_{i\rightarrow k})-2(ik\,|\,G\,|\,ki) \tag{6}$$

where,

$$(ik\,|\,G\,|\,ik)=\int\phi_i^*(1)\phi_k^*(2)\frac{e^2}{r_{12}}\phi_i(1)\phi_k(2)\,d\upsilon_1 d\upsilon_2 \tag{7}$$

$$(ik\,|\,G\,|\,ki)=\int\phi_i^*(1)\phi_k^*(2)\frac{e^2}{r_{12}}\phi_k(1)\phi_i(2)\,d\upsilon_1 d\upsilon_2 \tag{8}$$

Expanding ϕ_i's in terms of AO's, and neglecting the differential overlap, Eqs. 7 and 8 become as follows,

$$(ik\mid G\mid ik)=\sum_{\mu,\nu} c^*_{i\mu}c_{i\mu}c^*_{k\nu}c_{k\nu}\gamma_{\mu\nu}\,, \tag{9}$$

$$(ik\mid G\mid ki)=\sum_{\mu,\nu} c^*_{i\mu}c_{k\mu}c^*_{k\nu}c_{i\nu}\gamma_{\mu\nu}\,. \tag{10}$$

ε_i and $E(\chi_{i\rightarrow k})$ thus calculated for nitrogen heterocycles may be different from the corresponding quantities of the parent hydrocarbon by small amounts $\delta\varepsilon_i$ and $\delta E(\chi_{i\rightarrow k})$, because of slight changes in the core potential and electronic repulsion energies due to the hetero-replacement.

The expressions for $\delta\varepsilon_i$ and $\delta E(\chi_{i\rightarrow k})$ may be written as follows

$$\delta\varepsilon_i=\sum_{\mu,\nu} c^*_{i\mu}c_{i\nu}(\delta F_{\mu\nu}) \tag{11}$$

$$\delta F_{\mu\mu}=\delta\alpha_\mu+\frac{1}{2}P_{\mu\mu}(\delta\gamma_{\mu\mu}) \tag{12}$$

$$\delta F_{\mu\nu}=\delta\beta_{\mu\nu}-\frac{1}{2}P_{\mu\nu}(\delta\gamma_{\mu\nu}) \tag{13}$$

$$\delta E(^1\chi_{i\rightarrow k})=\delta\varepsilon_k-\delta\varepsilon_i-\sum_{\mu,\nu} c^*_{i\mu}c_{i\mu}c^*_{k\nu}c_{k\nu}(\delta\gamma_{\mu\nu}) +2\sum_{\mu,\nu} c^*_{i\mu}c_{k\mu}c^*_{k\nu}c_{i\nu}(\delta\gamma_{\mu\nu}) \tag{14}$$

1) N. Mataga and K. Nishimoto, *Z. physik. Chem.*, N. F. in press.
2) N. Mataga, This Bulletin **31**, 453 (1958).
3) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 61 (1951).
4) R. McWeeny, *Proc. Phys. Soc.*, **A70**, 593 (1957).
5) We have calculated the electronic spectra of some unsaturated hydrocarbons by the self-consistent field method, using our semiempirical parameters described in refs. 1) and 2). N. Mataga and K. Nishimoto, to be published elsewhere.

$$\delta E(^3\chi_{i\to k}) = \delta E(^1\chi_{i\to k}) - 2\sum_{\mu,\nu} c^*_{i\mu}c_{k\mu}c^*_{k\nu}c_{i\nu}(\delta\gamma_{\mu\nu}) \quad (15)$$

In addition, we have taken into consideration some amount of configuration intereactions, which is restricted only to those invoked in the calculation of parent hydrocarbon.

The interconfigurational matrix elements may be expressed as follows.

$$(^1\chi_{i\to k}|\mathbf{H}|^1\chi_{j\to l}) = -(jk|G|il) + 2(jk|G|li) \quad (16)$$

$$(^3\chi_{i\to k}|\mathbf{H}|^3\chi_{j\to l}) = (^1\chi_{i\to k}|\mathbf{H}|^1\chi_{j\to l}) - 2(jk|G|li) \quad (17)$$

where,
$$(jk \mid G \mid il) = \sum_{\mu,\nu} c^*_{j\mu}c_{i\mu}c^*_{k\nu}c_{l\nu}\gamma_{\mu\nu}\ , \quad (18)$$

$$(jk \mid G \mid li) = \sum_{\mu,\nu} c^*_{j\mu}c_{l\mu}c^*_{k\nu}c_{i\nu}\gamma_{\mu\nu}\ . \quad (19)$$

The difference between these quantities and the corresponding ones of the parent hydrocarbon may be written as

$$\delta(^1\chi_{i\to k} \mid \mathbf{H} \mid {}^1\chi_{j\to l}) = -\sum_{\mu,\nu} c^*_{j\mu}c_{i\mu}c^*_{k\nu}c_{l\nu}(\delta\gamma_{\mu\nu}) + 2\sum_{\mu,\nu} c^*_{j\mu}c_{l\mu}c^*_{k\nu}c_{i\nu}(\delta\gamma_{\mu\nu}) \quad (20)$$

$$\delta(^3\chi_{i\to k} \mid \mathbf{H} \mid {}^3\chi_{j\to l}) = \delta(^1\chi_{i\to k} \mid \mathbf{H} \mid {}^1\chi_{j\to l}) - 2\sum_{\mu,\nu} c^*_{j\mu}c_{l\mu}c^*_{k\nu}c_{i\nu}(\delta\gamma_{\mu\nu}) \quad (21)$$

It will be shown in the next paragraph that $\delta\varepsilon_i$, $\delta E(_{i\to k})$ and $\delta(\chi_{i\to k} \mid \mathbf{H} \mid \chi_{j\to l})$ are really very small and only a small percent of ε_i, $E(\chi_{i\to k})$ and $(\chi_{i\to k} \mid \mathbf{H} \mid \chi_{j\to l})$, respectively.

Therefore, our present treatment may be regarded also as a kind of perturbation theory*.

Previously, Pariser and Parr[6] calculated the electronic spectra of some nitrogen heterobenzenes by their semiempirical ASMO method including configuration interaction, using, however, MO's of benzene.

Our procedure described above may be equivalent to theirs, but ours is in terms of Hartree-Fock SCF theory, involving configuration interaction. In view of the approximate nature of our treatment and also for lack of experimental data, values of $\gamma_{\mu\nu}$ necessary for the evalution of electronic repulsion integrals $\gamma_{\mu\nu}$ and oscillator strengths are taken from those of naphthalene. The method of the semiempirical evalution of $r_{\mu\nu}$ and the calculation of oscillator strength are the same as in the previous reports[1,2].

Results and Discussions

In Table I, the orbital energies of highest and second highest occupied levels and lowest and second lowest vacant levels which are responsible for transitions to lower excited states, are given together with their $\delta\varepsilon_i$.

In the case of isoquinoline, all levels are more or less depressed; in the case of quinoline, however, fourth and sixth levels are depressed on the one hand and fifth and seventh levels are lifted on the other hand. The perturbation caused by the hetero-replacement on α-position is different from that on β-position, in this way.

TABLE I*
(in unit of $e.v.$)

	Quinoline		Isoquinoline	
i	ε_i	$\delta\varepsilon_i$	ε_i	$\delta\varepsilon_i$
4	−10.791	−0.205	−11.196	−0.611
5	− 9.494	0.120	− 9.767	−0.153
6	− 2.734	−0.348	− 2.518	−0.133
7	− 1.209	0.205	− 1.442	−0.027

* $\delta\varepsilon_i = \varepsilon_i - \varepsilon^0_i$, where ε^0_i is the corresponding orbital energy of naphtalene.

In the following, we shall give a detailed account only about the transition to the lowest excited singlet state, the intensity of which is most remarkably influenced by the hetero-replacement. We shall also give some arguments on the corresponding triplet state, i. e. ^3L_b, in relation to the mechanism of fluorescence quenching in quinoline.

The excited state wave functions, energies of configurations and the values of interconfigulational matrix elements as well as their differences from the corresponding quantities of the parent hydrocarbon are given in Table II.

In Table III, the calculated excitation energies and oscillator strengths indicated in comparison with the observed values.

The calculated values of excitation energies are in a satisfactory agreement with observed ones and the slight difference between the observed spectra of quinoline and isoquinoline is well interpreted, i. e., the theory predicts that the excitation energy of isoquinoline is slightly smaller than that of quinoline, in agreement with the observation.

The experimental values of oscillator strengths of these molecules are uncertain, and only the values of $\log \varepsilon_{max}$ are given in Table III.

By an inspection of this table, the observed intensity of quinoline seems almost the same as that of isoquinoline. The ^1L_b band of quinoline, however, is strongly superposed by ^1L_b band, the intensity of which may be scarcely affected by the hetero-replacement*, in contradistinction to the case of isoquinoline, where the superposition is not so much remarkable

* The present writer is now pursuing a calculation on the electronic structure of nitrogen heterocycles, which is based on stadard method of the perturbation theory.

6) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

* The results for ^1L_a state together with those for ^1B_b and ^1B_a states will be published shortly.

TABLE II

(in units of *e. v.*)

Quinoline

$$\Psi(^1L_b) = 0.757\,{}^1\chi_{4\to6} - 0.652\,{}^1\chi_{5\to7}, \qquad E(^1\chi_{4\to6}) = 4.864, \qquad E(^1\chi_{5\to7}) = 5.092$$

$$\Psi(^3L_b) = 0.537\,{}^3\chi_{4\to6} - 0.843\,{}^3\chi_{5\to7}, \qquad E(^3\chi_{4\to6}) = 3.857, \qquad E(^3\chi_{5\to7}) = 4.085$$

$$(^1\chi_{4\to6} \mid \mathbf{H} \mid {}^1\chi_{5\to7}) = 0.763, \qquad (^3\chi_{5\to6} \mid \mathbf{H} \mid {}^3\chi_{5\to7}) = -0.244.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{4\mu}c^*_{6\nu}c_{6\nu}\gamma_{\mu\nu} = \sum_{\mu,\nu} c^*_{5\mu}c_{5\mu}c^*_{7\nu}c_{7\nu}\gamma_{\mu\nu} = 4.199,$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{6\nu}c_{4\nu}\gamma_{\mu\nu} = \sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu} = 0.503.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu} = \sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu}, \qquad \sum_{\mu,\nu} c^*_{4\mu}c_{5\mu}c^*_{7\nu}c_{6\nu}\gamma_{\mu\nu} = 0.244.$$

$$\delta E(^1\chi_{4\to6}) = -0.176, \qquad \delta E(^1\chi_{5\to7}) = 0.052, \qquad \delta(^1\chi_{4\to6} \mid \mathbf{H} \mid {}^1\chi_{5\to7}) = 0.000,$$

$$\delta E(^3\chi_{4\to6}) = -0.149, \qquad \delta E(^3\chi_{5\to7}) = 0.079, \qquad \delta(^3\chi_{4\to6} \mid \mathbf{H} \mid {}^3\chi_{5\to7}) = 0.003.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{4\mu}c^*_{6\nu}c_{6\nu}(\delta\gamma_{\mu\nu}) = \sum_{\mu,\nu} c^*_{5\mu}c_{5\mu}c^*_{7\nu}c_{7\nu}(\delta\gamma_{\mu\nu}) = 0.033.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{6\nu}c_{4\nu}(\delta\gamma_{\mu\nu}) = \sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}(\delta\gamma_{\mu\nu}) = 0.000.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{5\mu}c^*_{7\nu}c_{6\nu}(\delta\gamma_{\mu\nu}) = 0.000.$$

Isoquinoline

$$\Psi(^1L_b) = 0.410\,{}^1\chi_{4\to6} - 0.911\,{}^1\chi_{5\to7}, \qquad E(^1\chi_{4\to6}) = 5.513, \qquad E(^1\chi_{5\to7}) = 4.101$$

$$\Psi(^3L_b) = 0.883\,{}^3\chi_{4\to6} - 0.469\,{}^3\chi_{5\to7}, \qquad E(^3\chi_{4\to6}) = 4.454, \qquad E(^3\chi_{5\to7}) = 3.043$$

$$(^1\chi_{4\to6} \mid \mathbf{H} \mid {}^1\chi_{5\to7}) = 0.798, \qquad (^3\chi_{4\to6} \mid \mathbf{H} \mid {}^3\chi_{5\to7}) - 0.260.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{4\mu}c^*_{6\nu}c_{6\nu}\gamma_{\mu\nu} = \sum_{\mu,\nu} c^*_{5\mu}c_{5\mu}c^*_{7\nu}c_{7\nu}\gamma_{\mu\nu} = 4.224.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{6\nu}c_{4\nu}\gamma_{\mu\nu} = \sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu} = 0.529.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu} = \sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}\gamma_{\mu\nu}, \qquad \sum_{\mu,\nu} c^*_{4\mu}c_{5\mu}c^*_{7\nu}c_{6\nu}\gamma_{\mu\nu} = 0.260.$$

$$\delta E(^1\chi_{4\to6}) = 0.473, \qquad \delta E(^1\chi_{5\to7}) = -0.393, \qquad \delta(^1\chi_{4\to6} \mid \mathbf{H} \mid {}^1\chi_{5\to7}) = 0.035.$$

$$\delta E(^3\chi_{4\to6}) = 0.448, \qquad \delta E(^3\chi_{5\to7}) = 0.095, \qquad \delta(^3\chi_{4\to6} \mid \mathbf{H} \mid {}^3\chi_{5\to7}) = -0.013.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{4\mu}c^*_{6\nu}c_{6\nu}(\delta\gamma_{\mu\nu}) = \sum_{\mu,\nu} c^*_{5\mu}c_{5\mu}c^*_{7\nu}c_{7\nu}(\delta\gamma_{\mu\nu}) = 0.058.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{6\mu}c^*_{6\nu}c_{4\nu}(\delta\gamma_{\mu\nu}) = \sum_{\mu,\nu} c^*_{5\mu}c_{7\mu}c^*_{7\nu}c_{5\nu}(\delta\gamma_{\mu\nu}) = 0.026.$$

$$\sum_{\mu,\nu} c^*_{4\mu}c_{5\mu}c^*_{7\nu}c_{6\nu}(\delta\gamma_{\mu\nu}) = 0.016.$$

TABLE III

	Excitation Energy (*e.v.*)		Oscillator Strength	
	Calcd.	Obsd.[a,b]	Calcd.	Obsd.[a] ($\log \varepsilon_{max}$)
	Quinoline			
^1L_b	4.207	3.96	0.01	3.4
^3L_b	4.240	—	0.00	—
	Isoquinoline			
^1L_b	3.742	3.86	0.16	3.6
^3L_b	4.592	—	0.00	—

a) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds", John Wiley and Sons, 1951.

b) J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).

because ^1L_a band is shifted to a somewhat shorter wave length side and ^1L_b band to a longer wave length side in some degree compared with those of quinoline.

Therefore, in reality, the oscillator strength of quinoline may be far smaller than that of isoquinoline, in qualitative agreement with the theoretical prediction. Now, some considerations on the mechanism of the fluorescence quenching in nitrogen heterocycles will be given on the basis of the present theoretical calculation. Previously, we have studied the hydrogen bonding effect on the fluorescence of quinoline and acridine in non-polar solvent mixed with various proton donors, in order to elucidate the mechanism of inner quenching in these molecules[7]. The results were as follows. The larger the relative fluorescence yields of hydrogen bonded nitrogen heterocycles become, the stronger the donating powers of proton donors are, and from this fact, it has become clear that the cause of the remarkable inner quenching in these molecules compared with the parent aromatic hydrocarbons may be attributable to the interaction between n- and π-electrons in the

7) N. Mataga and S. Tsuno, This Bulletin, **30**, 368 (1957).

excited state, which may probably induce the radiationless transition to the ground state, directly or indirectly.

Moreover, we have found an interesting fact that the difference in the emitting π-electronic state leads to the different behavior of these nirogen heterocycles in fluorescene quenching by a halogen atom.

Although the increase in fluorescence yields of quinoline and acridine by hydrogen bonding with ethanol or by proton addition in aqueous solution is almost the same, the fluorescence yield of quinoline hydrogen bonded with trichloracetic acid is rather small compared with the fluorescence yield in ethanol solution, in contradistinction to the fact that the fluorescence yield of acridine is greatly enhanced by hydrogen bonding with trichloracetic acid. This distinction in these two molecules was ascribsd to the difference of emitting π-electronic state as follows[7].

In aromatic hydrocarbons, such as benzene, naphthalene and anthracene, there exists ^3L_b state which has the same energy as ^1L_b, but for ^1L_a, there exists no such circumstance, the energy of ^3L_a state being considerably different from that of ^1L_a[5,8,9]. If the lowest singlet excited state is ^1L_b, the phosphorescence transition occurs with relative ease probably by the process, $^1L_b \rightarrow {}^3L_b \rightarrow {}^3L_a \rightarrow$ ground state. However, when the lowest singlet excited state is ^1L_a, phosphorescence transition may be very difficult. We have assumed[7] that the analogous situation probably prevails also in these heterocyclic molecules, because of the close similarity of the electronic spectra of the latter with those of isoelectronic aromatic hydrocarbons. Now, as shown in Table III, the results of the present calculation clearly indicate that, at least in the case of quinoline, there exists ^3L_b state which has almost the same energy as ^1L_b. Thus, on the basis of the present results, it is confirmed that, at least in the case of quinoline, the near-by existence of a halogen atom may easily accelerate $^1L_b \rightarrow {}^3L_b$ process owing to the spin orbital perturbation, but it may be difficult for such a situation to be realized in acridine*. The circumstance in the case of isoqunoline may be somewhat different from the situation described above, because ^3L_b is somewhat higher than ^1L_b. Unfortunately, such an experimental observation for the case of isoquinoline is not yet available. After all, the close spectral similarity of quinoline and isoquinoline with naphthalene and also the intensification of ^1L_b band due to heteroreplacement are well comprehended by the present perturbation method. Moreover, the assumed effect of emitting π-electronic state on the quenching phenomenon, has been confirmed on the theoretical ground.

8) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).
9) J. A. Pople, *Proc. Phys, Soc.*, **68A**, 81 (1955).

* Detailed discussions on acridine will be given in a following paper.

Summary

1. A pertubation theory based on the Hartree-Fock SCF theory including a limited number of configuration interactions was applied to quinoline and isoquinoline.

2. The theory satisfactorily interprets the excitation energies and oscillator strengths of ^1L_b bands of these nitrogen heterocycles.

3. The previous assumption concerning the effect of π-electronic state on the fluorescence quenching in nitrogen heterocycles due to the near-by existence of a halogen atom, was confirmed for the case of quinoline, on the basis of the theoretical calculation.

The present author expresses his sincere gratitude to Professor S. Mizushima of Tokyo University for his encouragement. He is also gratful to Professor R. Fujishiro for his encouragement. He expresses his cordial thanks to Dr. S. Nagakura of Tokyo University, Dr. H. Tsubomura of Tokyo University and Dr. H. Baba of Hokkaido University for their fruitful discussions. He also is glad to express his appreciation to Mr. K. Nishimoto and Miss S. Tsuno for their helpful discussions.

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Electronic Spectra of Acridine and Phenazine

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In the first papar[1] of our studies on the electronic structure and spectra of nitrogen heterocycles, some semiquantitative treatments on the electronic spectra of acridine and phenazine have been given, on the basis of the results obtained for nitrogen heterobenzenes employing the Hartree-Fock SCF theory including the limited amount of configuration interactions. In the present report, we shall apply the perturbation method developed in the third paper[2] to these three-ring nitrogen heterocycles, and give more detailed and quantitative interpretations on the electronic structure and spectra of these molecules.

Electronic Spectra of Anthracene as a Basis of the Perturbation Calculation

As a first step, we have regarded the naive MO's of anthracene as a good approximation to the MO's of these three ring nitrogen heterocycles. As pointed out by Dewar and Longuet-Higgins[3] in their semiquantitative discussions on the general feature of aromatic hydrocarbon spectra, the naive MO's of these aromatic hydrocarbons may be good approximate solutions of the Hartree-Fock self-consistent field equations or close to the best MO's available for constructing the excited state wave functions, owing to the uniformity of electron distribution in these molecules.

In our theoretical work[4] on the electronic spectra of some unsaturated hydrocarbons, it has been clearly indicated, that, for example, employing our semi-empirical parameters,[1,5] the naive MO's of naphthalene interpret the experimental spectra almost equally well as the Hartree-Fock self-consistent field MO's and also the approximate self-consistent field MO's obtained by neglecting the non-diagonal matrix elements of Fock's Hamiltonian in terms of AO's, $F_{\mu\nu}$, when μ and ν are apart each other further than the nearest neighbor. Thus, in this case, naive MO's are very satisfactory for the description of electronic spectra, although they give a wrong prediction about the bond orders in the ground state.

The naive MO's of anthracene also give a satisfactory explanation of the experimental spectra as in the following cases.

In view of the approximate nature of our treatment, the geometrical structure of the molecule has been assumed to be a condensed regular hexagon, the nearest neighbor bond distance of which has been taken as 1.402_7 Å. This value is a weighted mean of five different bond distances determined by X-ray diffraction[6]. The same geometrical structure as anthracence, has been assumed also for acridine and phenazine treated in a latter paragraph.

The MO's and MO energies of anthra-

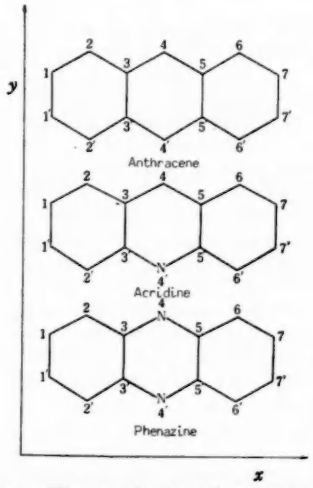

Fig. 1. The numbering of atoms and the coordinate of symmetry operation.

1) N. Mataga and K. Nishimoto, *Z. Phys. Chem.* N. F., in press.
2) N. Mataga, to be published in this Bulletin.
3) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc.*, **67A**, 795 (1954).
4) N. Mataga and K. Nishimoto, to be published elsewhere.
5) N. Mataga, to be published in this Bulletin.
6) J. M. Robertson, "Organic Crystals and Molecules", Cornell University Press, 1953.

TABLE I

MO's AND MO ENERGIES OF ANTHRACENE

Symmetry	ε_i(*e.v.*)	
b_{1g}	−10.4865	$\psi_6=0.3535\sigma_6+0.3535\sigma_7$
b_{3g}	− 8.8987	$\psi_7=0.3109\sigma_8+0.2199\sigma_9+0.0911\sigma_{10}-0.4397\sigma_{11}$
b_{2u}	− 3.1013	$\psi_8=0.3109\sigma_1-0.2199\sigma_2+0.0911\sigma_3-0.4397\sigma_4$
a_{1u}	− 1.5135	$\psi_9=-0.3535\sigma_{13}+0.3535\sigma_{14}$

$\sigma_1=(\phi_6+\phi_{6'}+\phi_2+\phi_{2'})$, $\sigma_2=(\phi_7+\phi_{7'}+\phi_{1'}+\phi_1)$, $\sigma_3=(\phi_{3'}+\phi_3+\phi_5+\phi_{5'})$, $\sigma_4=(\phi_4+\phi_{4'})$

$\sigma_8=(\phi_6-\phi_{6'}+\phi_2-\phi_{2'})$, $\sigma_6=(\phi_7+\phi_{7'}-\phi_{1'}-\phi_1)$, $\sigma_7=(\phi_{3'}+\phi_3-\phi_5-\phi_{5'})$, $\sigma_{11}=(\phi_4-\phi_{4'})$

$\sigma_9=(\phi_7-\phi_{7'}-\phi_{1'}+\phi_1)$, $\sigma_{10}=(\phi_{3'}-\phi_3-\phi_5+\phi_{5'})$,

$\sigma_{13}=(\phi_7-\phi_{7'}+\phi_{1'}-\phi_1)$, $\sigma_{14}=(\phi_{3'}-\phi_3+\phi_5-\phi_{5'})$,

TABLE II*

THE EXCITED STATE WAVE FUNCTIONS, ENERGIES OF CONFIGURATIONS AND THE VALUES OF INTERCONFIGURATIONAL MATRIX ELEMENTS OF ANTHRACENE

$\Psi(^1B^+_{1u})=0.9875\,{}^1\chi_{7\to8}+0.1576\,{}^1\chi_{6\to9}$, $E(^1\chi_{7\to8})=3.5549$,

$\Psi(^1B^-_{1u})=0.1576\,{}^1\chi_{7\to8}-0.9875\,{}^1\chi_{6\to9}$, $E(^1\chi_{6\to9})=6.3681$,

$\Psi(^3B^+_{1u})=0.9986\,{}^3\chi_{7\to8}+0.0516\,{}^3\chi_{6\to9}$, $E(^3\chi_{7\to8})=1.6999$,

$\Psi(^3B^-_{1u})=0.0516\,{}^3\chi_{7\to8}-0.9986\,{}^3\chi_{6\to9}$, $E(^3\chi_{6\to9})=4.8158$.

$(78\mid G\mid 78)=4.0975$, $(78\mid G\mid 87)=0.9275$, $(68\mid G\mid 79)=0.1616$,

$(69\mid G\mid 69)=4.1572$, $(69\mid G\mid 96)-0.7761$, $(68\mid G\mid 97)=-0.1496$.

$$\Psi(^1B^+_{3u})=\frac{1}{\sqrt{2}}(^1\chi_{6\to8}+{}^1\chi_{7\to9}),\qquad E(^1\chi_{6\to8})=E(^1\chi_{7\to9})=4.5470$$

$$\Psi(^1B^-_{3u})=\frac{1}{\sqrt{2}}(^1\chi_{6\to8}-{}^1\chi_{7\to9}),$$

$$\Psi(^3B^+_{3u})=\frac{1}{\sqrt{2}}(^3\chi_{6\to8}+{}^3\chi_{7\to9}),\qquad E(^3\chi_{6\to8})=E(^3\chi_{7\to9})=3.7472$$

$$\Psi(^3B^-_{3u})=\frac{1}{\sqrt{2}}(^3\chi_{6\to8}-{}^3\chi_{7\to9}),$$

$(68\mid G\mid 68)=(79\mid G\mid 79)=3.6380$, $(68\mid G\mid 86)=(79\mid G\mid 97)=0.3999$,

$(78\mid G\mid 69)=(68\mid G\mid 79)$, $(78\mid G\mid 96)=(68\mid G\mid 86)$.

$(^1\chi_{7\to8}\mid \mathbf{H}\mid {}^1\chi_{6\to9})=(^1\chi_{6\to8}\mid \mathbf{H}\mid {}^1\chi_{7\to9})=-0.4608$.

$(^3\chi_{7\to8}\mid \mathbf{H}\mid {}^3\chi_{6\to9})=(^3\chi_{6\to8}\mid \mathbf{H}\mid {}^3\chi_{7\to9})=-0.1616$.

* in units of *e.v.*

cene, which concern the electronic transitions to lower excited states are given in Table I.

The numbering of atoms and the coordinate of symmetry operation are shown in Fig. 1. In the approximation of naive MO theory, $\psi_6(b_{1g})$ and $\psi_5(a_{1u})$ are degenerate accidentally in the occupied orbitals as well as $\psi_9(a_{1u})$ and $\psi_{10}(b_{1g})$ in the vacant orbitals. The inclusion of electron interaction, however, removes this accidental degeneracy, and a_{1u} is the lower both in occupied and vacant orbitals. The excited state wave functions, energies of configurations and the values of interconfigurational matrix elements are given in Table II.

The calculated excitation energies and oscillator strengths are collected in Table III, in comparison with the observed values. By an inspection of this table, one may be allowed to say that the theoretical predictions are in very good agreement with the experimental observation, in view of the approximate nature of our calculation.

TABLE III

CALCULATED AND OBSERVED EXCITATION ENERGIES AND OSCILLATOR STRENGTHS OF ANTHRACENE

Symmetry		Excitation Energy(*e.v.*)		Oscillator Strength	
Group theory	Platt	Calcd.	Obsd.	Calcd.	Obsd.[a]
$^1B^+_{1u}$	^1L_a	3.4813	3.30[a]	0.39	∼0.1
$^1B^-_{3u}$	^1L_b	3.9087	3.50[a]	0.00	∼0
$^1B^+_{3u}$	^1B_b	5.1853	4.80[a]	3.00	2.20
$^1B^-_{1u}$	^1B_a	6.4416	5.64[a]	0.81	0.65
$^3B^+_{1u}$	^3L_a	1.6915	1.8[b]	0.00	—
$^3B^+_{3u}$	^3B_b	3.5856	—	0.00	—
$^3B^-_{3u}$	^3L_b	3.9087	—	0.00	—
$^3B^-_{1u}$	^3B_a	4.8241	—	0.00	—

a) H. B. Klevens and J. R. Platt, *J. Chem. Phys.* **17**, 470 (1949).

b) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944); McGlynn, Padhye and Kasha, *J. Chem. Phys.*, **23**, 593 (1955).

Now, let us examine the spectra of heterocycles, on the basis of these results.

Acridine and Phenazine

The orbital energies for acridine and phenazine are collected in Table IV, and Tables V and VI correspond to Tables II and III of the preceding paragraph respectively.

TABLE IV.

ORBITAL ENERGIES OF ACRIDINE AND PHENAZINE

i	ε_i(e.v.)	
	acridine	phenazine
6	−10.4865	−10.4865
7	− 9.3459	− 9.7924
8	− 3.9069	− 3.7815
9	− 1.5135	− 1.5135

The agreement between the calculated and the observed values of excitation energies and oscillator strengths is fairly good in general, although the error between calculated and observed energies of ^1L_a band of phenazine is considerable. About this inconsistency, a more detailed treatment is given in the latter part of this paper. The behavior of ^1L_b band, however, is well comprehended with the above results.

The cause of the intensification of ^1L_b band has been ascribed to the inequality of the coefficients a and b in Eq. 1, in the case of nitrogen heterobenzenes[1,5] and monoazanaphthalenes[2].

$$\Psi(^1L_b) = a^1\chi_{i\to k} + b^1\chi_{j\to l} \tag{1}$$

The ratio of the coefficients in Eq. 1 is correlated to the energies of configurations and the interconfigurational matrix element by

$$\frac{a}{b} = \frac{2(^1\chi_{i\to k} \mid \mathbf{H} \mid {}^1\chi_{j\to l})}{[\{E(^1\chi_{i\to k}) - E(^1\chi_{j\to l})\}^2 + 4(^1\chi_{i\to k} \mid \mathbf{H} \mid {}^1\chi_{j\to l})^2]^{1/2} - \{E(^1\chi_{i\to k}) - E(^1\chi_{j\to l})\}} \tag{2}$$

TABLE V*

THE EXCITED STATE WAVE FUNCTIONS, ENERGIES OF CONFIGURATIONS AND THE VALUES OF INTERCONFIGURATIONAL MATRIX ELEMENTS OF ACRIDINE AND PHENAZINE

$\Psi(^1A^+_1) = 0.9892^1\chi_{7\to8} + 0.1461^1\chi_{6\to9}$, $E(^1\chi_{7\to8}) = 3.2367$,
$\Psi(^1A^-_1) = 0.1461^1\chi_{7\to8} - 0.9892^1\chi_{6\to9}$, $E(^1\chi_{6\to9}) = 6.3681$,
$\Psi(^3A^+_1) = 0.9990^3\chi_{7\to8} + 0.0450^3\chi_{6\to9}$, $E(^3\chi_{7\to8}) = 1.2357$,
$\Psi(^3A^-_1) = 0.0450^3\chi_{7\to8} - 0.9990^3\chi_{6\to9}$, $E(^3\chi_{6\to9}) = 4.8158$.
$(78 \mid G \mid 78) = 4.2033$, $(78 \mid G \mid 87) = 1.0005$, $(68 \mid G \mid 79) = 0.1616$,
$(69 \mid G \mid 69) = 4.1572$, $(69 \mid G \mid 96) = 0.7761$, $(68 \mid G \mid 97) = -0.1556$.
$(^1\chi_{7\to8} \mid \mathbf{H} \mid {}^1\chi_{6\to9}) = -0.4728$, $(^3\chi_{7\to8} \mid \mathbf{H} \mid {}^3\chi_{6\to9}) = -0.1616$.
$\Psi(^1B^+_1) = 0.3870^1\chi_{6\to8} + 0.9221^1\chi_{7\to9}$, $E(^1\chi_{6\to8}) = 3.7182$,
$\Psi(^1B^-_1) = 0.9221^1\chi_{6\to8} - 0.3870^1\chi_{7\to9}$, $E(^1\chi_{7\to9}) = 4.6170$,
$\Psi(^3B^+_1) = 0.9920^3\chi_{6\to8} + 0.1259^3\chi_{7\to9}$, $E(^3\chi_{6\to8}) = 2.9184$,
$\Psi(^3B^-_1) = 0.1259^3\chi_{6\to8} - 0.9920^3\chi_{7\to9}$, $E(^3\chi_{7\to9}) = 4.1712$.
$(68 \mid G \mid 68) = (79 \mid G \mid 79) = 3.6612$, $(78 \mid G \mid 96) = (68 \mid G \mid 86)$,
$(68 \mid G \mid 86) = (79 \mid G \mid 97) = 0.3999$, $(78 \mid G \mid 69) = (68 \mid G \mid 79)$.
$(^1\chi_{6\to8} \mid \mathbf{H} \mid {}^1\chi_{7\to9}) = 0.6382$, $((^3\chi_{6\to8} \mid \mathbf{H} \mid {}^3\chi_{7\to9}) = -0.1616$.

Phenazine

$\Psi(^1B^+_{1u}) = 0{\cdot}9831^1\chi_{7\to8} + 0.1828^1\chi_{6\to9}$, $E(^1\chi_{7\to8}) = 3.8507$,
$\Psi(^1B^-_{1u}) = 0.1828^1\chi_{7\to8} - 0.9831^1\chi_{6\to9}$, $E(^1\chi_{6\to9}) = 6.3681$,
$\Psi(^3B^+_{1u}) = 0.9986^3\chi_{7\to8} + 0.0517^3\chi_{6\to9}$, $E(^3\chi_{7\to8}) = 1.7025$,
$\Psi(^3B^-_{1u}) = 0.0517^3\chi_{7\to8} - 0.9986^3\chi_{6\to9}$, $E(^3\chi_{6\to9}) = 4.8158$.
$(78 \mid G \mid 78) = 4.3084$, $(78 \mid G \mid 87) = 1.0741$, $(68 \mid G \mid 79) = 0.1616$,
$(69 \mid G \mid 69) = 4.1572$, $(69 \mid G \mid 96) = 0.7761$, $(68 \mid G \mid 97) = -0.1616$.
$(^1\chi_{7\to8} \mid \mathbf{H} \mid {}^1\chi_{6\to9}) = -0.4849$, $(^3\chi_{7\to8} \mid \mathbf{H} \mid {}^3\chi_{6\to9}) = -0.1616$.
$\Psi(^1B^+_{3u}) = 0.3341^1\chi_{6\to8} + 0.9425^1\chi_{7\to9}$, $E(^1\chi_{6\to8}) = 3.8205$,
$\Psi(^1B^-_{3u}) = 0.9425^1\chi_{6\to8} - 0.3341^1\chi_{7\to9}$, $E(^1\chi_{7\to9}) = 5.3944$,
$\Psi(^3B^+_{3u}) = 0.9949^3\chi_{6\to8} + 0.1011^3\chi_{7\to9}$, $E(^3\chi_{6\to8}) = 3.0207$,
$\Psi(^3B^-_{3u}) = 0.1011^3\chi_{6\to8} - 0.9949^3\chi_{7\to9}$, $E(^3\chi_{7\to9}) = 4.5946$.
$(68 \mid G \mid 68) = (79 \mid G \mid 79) = 3.6843$, $(78 \mid G \mid 96) = (68 \mid G \mid 86)$,
$(68 \mid G \mid 86) = (79 \mid G \mid 97) = 0.3999$, $(78 \mid G \mid 69) = (68 \mid G \mid 79)$.
$(^1\chi_{6\to8} \mid \mathbf{H} \mid {}^1\chi_{7\to9}) = 0.6382$, $(^3\chi_{6\to8} \mid \mathbf{H} \mid {}^3\chi_{7\to9}) = -0.1616$.

* in units of e.v.

TABLE VI

CALCULATED AND OBSERVED EXCITATION ENERGIES AND OSCILLATOR STRENGTHS OF ACRIDINE AND PHENAZINE

Symmetry		Excitation Energy (*e.v.*)		Oscillator Strength	
Group throry	Platt	Calcd.	Obsd.	Calcd.	Obsd.
		Acridine			
$^1A^+_1$	^1L_a	3.1669	3.18[a]	0.36	*
$^1B^-_1$	^1L_b	3.4504	3.50[a]	0.29	*
$^1B^+_1$	^1B_b	5.2389	4.96[a]	2.61	*
$^1A^-_1$	^1B_a	6.4379	5.82[a]	0.79	*
$^3A^+_1$	^3L_a	1.2284	—	0.00	—
$^3B^+_1$	^3B_b	2.8979	—	0.00	—
$^3B^-_1$	^3L_b	4.1917	—	0.00	—
$^3A^-_1$	^3B_a	4.8231	—	0.00	—
		Phenazine			
$^1B^+_{1u}$	^1L_a	3.7605	3.09[b]	0.39	*
$^1B^-_{3u}$	^1L_b	3.5942	3.40[b]	0.38	*
$^1B^+_{3u}$	^1B_b	5.6206	4.95[b]	2.66	*
$^1B^-_{1u}$	^1B_a	6.4583	5.88[b]	0.85	*
$^3B^+_{1u}$	^3L_a	1.6941	—	0.00	—
$^3B^+_{3u}$	^3B_b	3.0043	—	0.00	—
$^3B^-_{3u}$	^3L_b	4.6110	—	0.00	—
$^3B^-_{1u}$	^3B_a	4.8241	—	0.00	—

a) V. Zanker, *Z. physikal. Chem.* N. F., **2**, 52 (1954).

b) H. H. Perkampus, ibid., **6**, 18 (1956) and N. Mataga, unpublished.

* The oscillator strengths of these molecules are uncertain. The intensification of ^1L_b band due to hetero-replacement is remarkable, and the oscillator stength of ^1L_b band may be almost equal to that of ^1L_a band, in its order of magnitude, and the oscillator strengths of ^1B_b and ^1B_a bands are approximately equal to those of anthracene, respectively.

When $(^1\chi_{i\to k} \mid \mathbf{H} \mid {}^1\chi_{j\to l})$ is constant, the inequality of a and b becomes more remarkable, the larger the difference of $E(^1\chi_{i\to k})$ and $E(^1\chi_{j\to l})$. This was the case in the series of benzene, pyridine and pyrazine[1], the inequality being increased in this order. Moreover, it is characteristic that, the larger the difference between $(\varepsilon_k-\varepsilon_i)$ and $(\varepsilon_l-\varepsilon_j)$, the greater is the $\{E(^1\chi_{j\to l})-E(^1\chi_{j\to l})\}$, viz., $2(ik \mid G \mid ki)-(ik \mid G \mid ik)$ is nearly equal to $2(jl\mid G\mid lj)-(jl\mid G\mid jl)$. It was assumed that, this circumstance in nitrogen heterobenzenes might also prevail in the ^1L_b bands of anthracene, acridine and phenazine. On this assumption, the observed intensities of ^1L_b bands in this series of molecules were discussed qualitatively.[1]

From Tables II, V and VI, it is evident that, our previous assumption is almost exactly valid in the approximation of the present calculation, and accordingly the observed intensities are well comprehended by such a consideration. In contradistinction to ^1L_a band, which suffers the red shift by the heteroreplacement, the position of ^1L_b band is almost invariable in this series of molecules. This situation can be interpreted similarly to the case of nitrogen heterobenzenes.[1,5] The two configurations $^1\chi_{6\to8}$ and $^1\chi_{7\to9}$ are degenerate in anthracene, although they are split in the case of acridine and phenazine, the degree of splitting being larger in phenazine. As shown in Tables II, III, V and VI, however, the energy depression due to the configuration interaction is most remarkable in the case of anthracene and it becomes smaller in acridine and phenazine in this order causing the approximate invariance of the excitation energy of ^1L_b band in this series of molecules. Thus, the observed excitation energy and oscillator strength of ^1L_b band in these molecules are well interpreted by the present calculation. Now, the cause of the reversal of the relative order in the calculated energy of ^1L_a and ^1L_b states, in the case of phenazine, may probably be attributable to the inadequacy of the MO's used.

As is pointed out previously,[1,5] the Hartree-Fock self-consistent field MO's of nitrogen heterobenzenes are fairly close to the naive MO's obtained by putting α_N, the Coulomb integral at the nitrogen atom, to be equal to $\alpha+0.5\beta$. Extending this result to the present case, we have calculated the naive MO's of phenazine as shown in Table VII, where only the MO's concerning the lower excited states are indicated.

In terms of these MO's, the excitation

TABLE VII*

MO's AND MO ENERGIES OF PHENAZINE ($\alpha_N=\alpha+0.5\beta$)

Symmetry	ε_i (*e.v.*)	
b_{1g}	−10.6821	$\psi_6=0.3535\sigma_6+0.3535\sigma_7$
b_{3g}	− 9.5282	$\psi_7=0.3557\sigma_8+0.2244\sigma_9+0.0162\sigma_{10}-0.3816\sigma_{11}$
b_{2u}	− 3.6398	$\psi_8=0.2636\sigma_1-0.2182\sigma_2+0.1632\sigma_3-0.4609\sigma_4$
a_{1u}	− 1.7233	$\psi_9=-0.3535\sigma_{13}+0.3535\sigma_{14}$

* The definitions of σ's are the same as those of anthracene.

energies, and oscillator strengths have been computed. The results are collected in Table VIII.

TABLE VIII
CALCULATED EXCITATION ENERGIES AND OSCILLATOR STRENGTHS OF PHENAZINE
(MO's: $\alpha_N=\alpha+0.5\beta$)

Symmetry		Excitation Energy ($e.v.$)	Oscillator Strength
Group theory	Platt		
$^1B^+_{1u}$	^1L_a	3.5142	0.34
$^1B^-_{3u}$	^1L_b	3.9122	0.20
$^1B^+_{3u}$	^1B_b	5.2439	2.84
$^1B^-_{1u}$	^1B_a	6.4294	0.80
$^3B^+_{1u}$	^3L_a	1.6958	0.00
$^3B^+_{3u}$	^3B_b	3.2523	0.00
$^3B^-_{3u}$	^3L_b	4.2029	0.00
$^3B^-_{1u}$	^3B_a	4.8087	0.00

As indicated in Table VIII, ^1L_a and ^1L_b bands are put in their right order, thus making the agreement with the experimental observation more satisfactory.

Eventually, the electronic spectra of acridine and phenazine, as well as those of quinoline and isoquinoline in the previous report[2], are well interpreted by our perturbation calculation, and the assignment of the spectra of three-ring nitrogen heterocycles, which was made in the first paper, has been given a more rigorous basis.

Summary

The electronic spectra of three-ring nitrogen heterocycles have been calculated by the perturbation method based on the Hartree-Fock self-consistent field theory. There is a satisfactory agreement in general between the calculated the and observed excitation energies and oscillator strengths, and the mechanism of the electronic transitions in these molecules has been discussed in detail.

The author is grateful to Professor S. Mizushima of Tokyo University for his encouragement. He is also indebted to Dr. S. Nagakura of Tokyo University, Dr. H. Tsubomura of Tokyo University and Dr. H. Baba of Hokkaido University for their valuable discussions. He expresses his appreciation to Professor R. Fujishiro for his encouragement, and also to Mr. K. Nishimoto and Miss S. Tsuno for their helpful discussions. He is also thankful to Miss S. Wada for typewriting this paper.

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A Study on the Micellar Solutions of Sodium Oleate and Elaidate

By Bun-ichi TAMAMUSHI, Michio SHIRAI and Kunio TAMAKI

(Received December 17, 1957)

Oleic and elaidic acid, which are known as geometrical isomers, have a certain difference in their physical and chemical properties such as their melting points. It is expected that the soaps of these isomers will behave themselves differently as regards the formation of micelles in solution. The examination of this probable difference will supply useful knowledge regarding the structure of micelles. There are already a good many data for the aqueous solutions of oleic acid salts but scarcely any for those of elaidic acid salts. The object of this work is to examine the effect of the geometrical isomerism on the formation and the structure of micelles by measuring the electrical conductivity, the interaction with a dye, the degree of hydrolysis, and the solubilizing power of aqueous solutions of sodium oleate (*cis* form) and elaidate (*trans* form). The dielectric polarization of *n*-heptane solutions of oleic and elaidic acid will also be determined in order to get information on the molecular association of these isomers.

Experimental

Procedure—The electrical conductivity was measured with the audio-frequency bridge of

Yokogawa & Co. using a frequency of 1000 cycles/sec., and the absorption spectrum with the spectrophotometer of Hitachi & Co.

For the measurement of pH of the solutions a glass electrode pH-meter was used.

The measurement of the dielectric constant was carried out by the method described in our previous paper[1].

Materials—Oleic acid was purified from the sample supplied by Armour & Co., U.S.A. by vacuum distillation. b.p. 202~203°C/5 mmHg. Elaidic acid was prepared by isomerization of oleic acid using nitrogen oxides as catalyst[2], and then extracted with petroleum ether. The product was recrystallized several times from ethanol.

Sodium oleate and elaidate were prepared by adding these acids to the ethanol solution of sodium hydroxide; the amount of the acids was taken slightly less than the amount calculated, the adjustment to neutrality being made with phenolphthalein as an external indicator. The neutral solutions obtained were evaporated under reduced pressure and the products were recrystallized from ethanol and dried in a vacuum desiccator.

Pinacyanol iodide was a pure sample supplied by Nezu Chemical Laboratory.

Benzene was washed with concentrated sulfuric acid, water, dilute sodium hydroxide solution and again with water. After distilling over calcium chloride, it was dried over metallic sodium, and then redistilled. *n*-Heptane was purified in the same way as benzene.

Results and Discussion

1) Electrical conductivity—In Table I and Fig. 1 are given the values of equivalent conductivity (Λ) as a function of the square root of molarity for sodium oleate and elaidate in water. The curves for these two salts are similar to each other as shown in Fig. 1. The result for sodium oleate is in good agreement with that obtained by Flockhart et al.[3] As seen in this figure, Λ increases steadily with decreasing concentration in a very low concentration range. Such a behavior has not been found with other paraffin-chain salts such as salts of higher alkyl sulfonic acids. The position of the breaking point is not clear, which may owe to the hydrolysis as found by Ekwall[4] and Preston[5]. But if we observe carefully the Λ—$\sqrt{C}$ curve in Fig. 1, we can detect a slight breaking point. Regarding this point as the critical point, the critical micelle concentration of sodium oleate and elaidate are 2.7×10^{-3} and 2.5×10^{-3} mole/l., respectively. Beyond such a critical point, the equivalent conductivity decreases with increasing concentration just as in the case of other paraffin-chain salts.

In Table I are shown the values of equivalent conductivity in aqueous ethanol of 2 mole/l. and 4 mole/l. For aqueous ethanol of 2 mole/l. the equivalent conductivity decreases slowly and the critical

TABLE I
EQUIVALENT CONDUCTIVITY

concn.	in water		in aq. ethanol of 2 mole/l.	in aq. ethanol of 4 mole/l.
	40°C	60°C	40°C	40°C
	sodium oleate			
0.0001	164	205	108.8	73.0
0.0002	150	194	102.0	71.2
0.0004	135	180	97.6	69.0
0.0007	123	167	93.6	68.0
0.001	113	157	92.3	68.0
0.0012	108	151	—	—
0.0015	104	149	90.0	68.5
0.0017	102	146	—	—
0.002	98.4	142	85.6	69.0
0.0025	95.6	137	80.0	69.5
0.003	91.7	132	76.4	69.2
0.004	—	—	72.4	67.4
0.005	75.4	112	—	—
0.006	—	—	65.6	65.2
0.008	—	—	59.5	63.0
0.01	61.9	89.6	56.0	61.6
0.02	53.6	73.6	48.0	54.8
0.05	46.3	67.4	41.8	45.6
0.1	43.2	63.6	—	—
	sodium elaidate			
0.0001	144	188	102.0	71.0
0.0002	132	180	99.0	68.7
0.0004	120	168	94.0	66.2
0.0007	113	159	91.4	66.8
0.001	110	155	89.5	67.5
0.0012	108	151	—	—
0.0015	106	148	84.1	68.0
0.0017	105	146	—	—
0.002	102	144	79.9	69.0
0.0025	97.2	142	76.0	69.5
0.003	89.3	131	72.5	68.6
0.004	—	—	69.0	67.0
0.005	71.0	102	65.9	—
0.006	—	—	62.5	63.3
0.008	—	—	57.4	60.6
0.01	54.7	80.4	53.9	58.3
0.02	46.4	67.6	45.8	49.5
0.05	39.9	55.8	35.4	42.3
0.1	38.0	53.9	—	—

1) M. Shirai and B. Tamamushi, This Bulletin, **30**, 542 (1957).
2) K. Fuse and B. Tamamushi, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **64**, 338 (1953).
3) B. D. Flockhart and H. Graham, *J. Colloid Sci.*, **8**, 105 (1953).
4) P. Ekwall, *Z. physik. Chem.*, **A161**, 198 (1932).
5) W. C. Preston, *J. Phys. & Colloid Chem.*, **52**, 84 (1948).

point is slightly shifted towards lower concentrations than in water, as shown in Fig. 2. For aqueous ethanol of 4 mole/l. the critical point becomes indistinct, the micelle formation being probably inhibited on account of the affinity of the solvent medium for the hydrocarbon chains of the soap molecules.

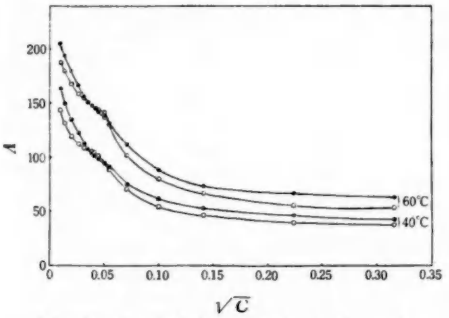

Fig. 1. Electrical conductivity in water. ●, sodium oleate; ○, sodium elaidate.

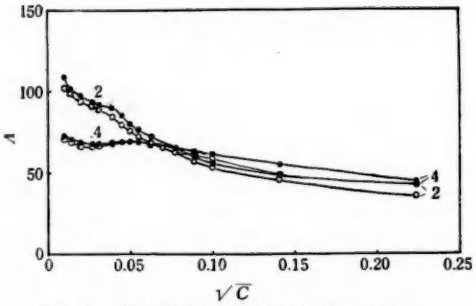

Fig. 2. Electrical conductivity in aqueous ethanol. Numbers on curves refer to the molarity of ethanol. ●, sodium oleate; ○, sodium elaidate.

In pure water the equivalent conductivity of sodium oleate is slightly greater than that of sodium elaidate at concentrations both below and beyond the critical micelle concentration except near that concentration, while in aqueous ethanol of 4 mole/l., where hydrolysis is reduced and the micelle formation is greatly inhibited, the equivalent conductivities of the two salts almost agree with each other. Therefore, it is conceivable that the smaller value of the equivalent conductivity of sodium elaidate is due to its greater power of micelle formation.

2) **Interaction with dye**—Sheppard and Geddes[6] found that, when pinacyanol salt is added to the solutions of surface active agents, its absorption spectrum changes at the critical micelle concentration. This experimental fact serves as a method of measurement of the critical micelle concentration[7]. Fig. 3 shows the optical density of solutions of pinacyanol iodide in sodium oleate and elaidate solution at an absorption maximum near 615 mμ as a function of the concentration of the salts. The critical rise of the optical density has been considered to be due to micelle formation, but the appearance of a minimum below the rise is yet unknown. From this figure we obtain 1×10^{-3} mole/l. as the critical micelle concentration for sodium oleate as well as for elaidate. However, as the concentration of the added dye appropriate for spectroscopic measurement is the same order of magnitude as those of the fatty acid salts, a considerable salt effect on the critical micelle concentration should be expected. Thus, the above obtained values of the critical micelle concentration must be considerably smaller than the true ones.

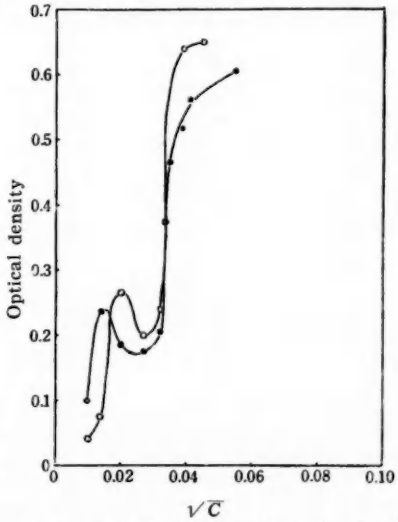

Fig. 3. Optical density of γ band of soap-pinacyanol iodide. ●, sodium oleate; ○, sodium elaidate.

3) **Hydrolysis**—The degree of hydrolysis (β), which is defined as the ratio of the concentration of hydroxyl ion generated by hydrolysis to that of total soap concentration, can be calculated from pH values. In Table II and Fig. 4 is indicated

6) S. E. Sheppard and A. L Geddes, *J. Chem. Phys.*, **13**, 63 (1945).

7) M. L. Corrin, H. B. Klevens and W. D. Harkins, ibid., **14**, 216 (1946).

TABLE II
DEGREE OF HYDROLYSIS

concn.	in water		in aq. ethanol of 2 mole/l.		in aq. ethanol of 4 mole/l.	
	pH	β (%)	pH	β (%)	pH	β (%)
			sodium oleate			
0.0001	7.56	1.10	7.30	0.60	7.25	0.54
0.0002	7.83	1.02	7.65	0.63	7.49	0.47
0.0004	8.10	0.95	8.08	0.91	7.65	0.34
0.0006	8.31	1.03	—	—	—	—
0.0007	—	—	8.43	1.15	7.80	0.27
0.0008	8.60	1.28	—	—	—	—
0.001	8.85	2.14	8.62	1.26	7.99	0.30
0·0015	—	—	8.85	1·43	8.12	0.27
0.002	9.40	3.80	8.97	1.42	8.32	0.32
0.0025	—	—	9.07	1.42	8.48	0.36
0.003	—	—	9.13	1.36	8.52	0.33
0.004	9.60	3.02	9.17	1.12	8.67	0.35
0.006	6.71	2.58	9.32	1.05	8.92	0.42
0.008	9.81	2.44	9.39	0.93	9.02	0.40
0.01	9.85	2.15	9.47	0.89	9.12	0.40
0.02	10.00	1.51	9.52	0.50	9.35	0.34
0.05	10.03	0.65	9.65	0.23	9.48	0.18
			sodium elaidate			
0.0001	7.80	1.90	—	—	7.65	1.14
0.0002	8.08	1.82	7.82	1.00	7.70	1.28
0.0004	8.42	1.99	8.35	1.21	7.75	0.91
0.0006	8.89	2.47	—	—	—	—
0.0007	—	—	8.52	1.43	7.80	0.64
0.0008	8.89	2.90	—	—	—	—
0.001	9.06	3.47	8.86	2.19	7.97	0.65
0.0015	—	—	9.08	2.40	8.27	0.58
0.002	9.67	7.05	9.21	2.45	8.40	0.47
0.0025	—	—	9.30	2.41	8.60	0.48
0.003	—	—	9.38	2.40	8.67	0.47
0.004	9.95	6.75	9.49	2.35	8.75	0.43
0.006	10.00	5.03	9.62	2.10	9.02	0.53
0.008	9.06	4.35	9.68	1.81	9.02	0.40
0.01	10.10	3.80	9.70	1.51	9.05	0.40
0.02	10.02	1.58	9.82	1.00	9.18	0.23
0.05	10.10	0.76	9.88	0.46	9.42	0.16

the result of the pH measurement, together with the degree of hydrolysis calculated therefrom. As shown in Fig. 4 the value of β decreases with increasing concentration and shows a minimum at some concentration below the critical micelle concentration. Then, it rises and reaches the maximum near the critical micelle concentration. Beyond that concentration it decreases gradually. The fact that a minimum and a maximum appear in $\beta-\sqrt{C}$ curve, has been explained by Stainsby and Alexander[8], and Cook[9] in relation to the micelle formation. They supposed that even below the critical micelle concentration submicelles could be formed. By submicelles are meant particles smaller than the well-recognized micelles but containing at least two molecules or ions per particle. The free acid molecules produced by hydrolysis will condense to submicelles, and accordingly, hydrolysis will go on further. With further increase in concentration of salts the counter ion association will take place and the micelle will be formed. At such concentrations the unhydrolyzed ions will condense to micelles too, and consequently, hydrolysis goes on no longer.

As is seen in Fig. 4 the concentrations

8) G. Stainsby and A. E. Alexander, *Trans. Faraday Soc.*, **45**, 585 (1949).
9) M. A. Cook, *J. Phys. & Colloid Chem.*, **55**, 383 (1951).

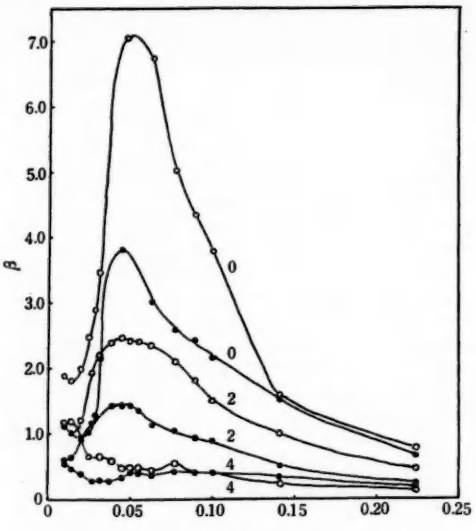

Fig. 4. Degree of hydrolysis in water and aqueous ethanol. Numbers on curves refer to the molarity of ethanol. ●, sodium oleate; ○, sodium elaidate.

where minimum and maximum of β appear for sodium oleate are nearly the same as for elaidate, while the value of β is much greater for sodium elaidate than for sodium oleate except at very large concentrations. This result is presumably due to the fact that sodium elaidate has a greater micelle forming power as well as a greater solubilization power for free acid than sodium oleate. Beyond the critical micelle concentration, β for each salt falls on nearly the same value.

In aqueous ethanol the maximum of β which is caused by hydrolysis and promoted by the submicelle formation becomes smaller. In aqueous ethanol of 4 mole/l., where the critical micelle concentration is not recognized by $\Lambda-\sqrt{C}$ curve, the maximum of β is almost diminished and β decreases monotonously with increasing concentration as in the case of ordinary electrolytes. These results obtained for the aqueous solutions and aqueous ethanol solutions correspond to the conductivity behavior of the salts, and support the view that the hydrolysis of the salts has a close relation with the micelle formation.

4) **Solubilization**—In Table III is given the experimental result of solubilization of benzene in terms of moles of solubilized benzene per mole of soap. It is shown that sodium elaidate has a greater solubilization power for benzene than sodium oleate, which is consistent with the result of pH measurement.

TABLE III
SOLUBILIZATION

substance	concn. of salt (mole/l.)	moles of benzene / mole of salt
sodium oleate	0.02	7.5
sodium elaidate	0.02	9.0
sodium oleate	0.1	12.5
sodium elaidate	0.1	15.0

5) **Dielectric polarization in nonpolar solvent.**—The experimental result of the measurement of dielectric polarization in *n*-heptane is shown in Table IV and Fig. 5, where x is the mole fraction, ε the dielectric constant, d the density, P_2 the molecular polarization of the solute, and μ the dipole moment. The electronic polarization P_E is computed from the atomic refraction and the atomic polarization P_A is assumed to be 5% of the electronic polarization. The molecular polarization decreases considerably with increasing concentration both for oleic and elaidic acid, but this decrease is slightly greater for elaidic acid than for oleic acid. This experimental fact shows that elaidic acid has a greater tendency towards association than oleic acid in a non-polar solvent. On the other hand, the molecular polarization at infinite dilution is nearly the same for both acids, and consequently, the dipole moment calculated

TABLE IV
DIELECTRIC POLARIZATION
n-heptane solution temp. 40°C

oleic acid

x	ε	d	P_2(cc.)
0.000000	1.9213	0.6709	(144.0)
0.003509	1.9272	0.6719	133.1
0.005808	1.9300	0.6726	126.2
0.009164	1.9325	0.6736	118.8
0.013354	1.9350	0.6750	112.7
0.018383	1.9377	0.6763	109.3

$P_E+P_A=90.7$ cc. $\mu=1.65$

elaidic acid

x	ε	d	P_2(cc.)
0.000000	1.9213	0.6709	(143.0)
0.002772	1.9262	0.6722	131.1
0.006295	1.9308	0.6736	120.5
0.009259	1.9335	0.6749	114.4
0.011743	1.9350	0.6757	111.4
0.016467	1.9386	0.6784	105.6

$P_E+P_A=90.7$ cc. $\mu=1.64$

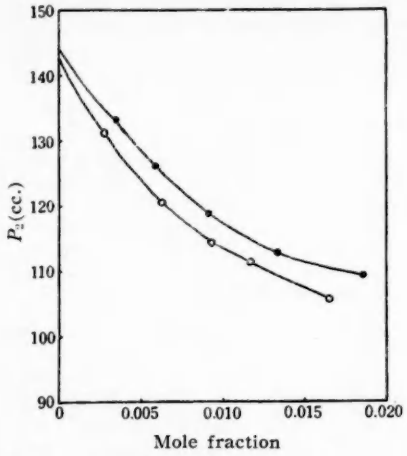

Fig. 5. Molecular polarization in *n*-heptane. ●, oleic acid; ○, elaidic acid.

from them is also nearly the same for both acids.

From these experimental results it is concluded that sodium elaidate has a slightly greater tendency towards association into micelles and a greater solubilization power for hydrocarbons, and accordingly has a greater degree of hydrolysis than sodium oleate.

Summary

The electrical conductivity, the interaction with pinacyanol iodide, the degree of hydrolysis, and solubilization power for benzene have been measured for sodium oleate and elaidate.

The conductivity behavior of these salts is consistent with the experimental result for hydrolysis and the latter result is also consistent with that of solubilization measurement. The result of dielectric polarization is also compatible with other results.

All these experimental results show that sodium elaidate has a slightly greater tendency towards micelle formation than sodium oleate.

We are indebted to the Ministry of Education for a reseach grant.

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*A New Analytical Method of Electroconductivity Data of Surfactant Solutions. III**

By Kenjiro MEGURO, Tamotsu KONDO and Noriaki OHBA

(Received February 1, 1958)

In previous papers[1,2] we have described that $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagram is better than Λ vs. $\sqrt{c}$ diagram to analyze the critical phenomena of a surfactant solution. In $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagram we were able to define two concentrations, C_{min} and C_{max}, which characterize the critical phenomena. We also discussed various effects—such as the effect of alkyl chain length,—on them. On the other hand, we found that the values of $(\Lambda_0-\Lambda)/\sqrt{c}$ at C_{min}, C_{max} and the gradient of $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curve between C_{min} and C_{max}, were very useful for analysis. These values were denoted by H_{min}, H_{max} and B.

In this paper we consider the meaning of these constants.

The meaning of C_{min} and C_{max}

Hartley and his associates[3] found the occurrence of a maximum equivalent conductivity in the aqueous solution of cetyl pyridonium chloride in a very high electric field. The C_{max} determined by our method in the case of cetyl pyridonium bromide corresponds to the concentration

* Presented at the 9th Annual Meeting of the Chemical Society of Japan held in Kyoto, April, 1956.

1) K. Meguro et al., This Bulletin **30**, 760 (1957).

2) K. Meguro et al., ibid., **30**, 905 (1957).

3) J. Malsh and G.S. Hartley, *Z. physik. Chem.*, **A140**, 321 (1934).

TABLE I

COMPARISON OF C_{min} AND C_{max} WITH THE TRANSPORT NUMBER DATA

Substance	C_{min}	Breaking pt. in Transport number vs. $\sqrt{c}$ curve	C_{max}	Level off pt. in Transport number vs. $\sqrt{c}$ curve
$C_8H_{17}NH_3Cl$	—	423	—	525
$C_{10}H_{21}NH_3Cl$	15.4	22.5	108	96
$C_{12}H_{25}NH_3Cl$	12.1	12.7	44.1	40.0
$C_{14}H_{29}NH_3Cl$	3.6	5.0	15.8	15.6
$C_{16}H_{33}NH_3Cl$	0.62	1.4	4.9	5.6
$C_{18}H_{37}NH_3Cl$	0.40	0.35	1.7	1.4

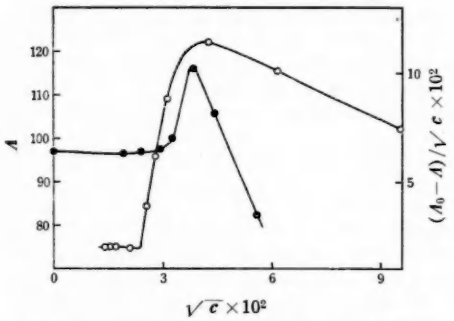

Fig. 1. Comparison of Λ vs. $\sqrt{c}$ curve for cetyl pyridonium chloride solution in high electric field (200 kV) with $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curve for cetyl pyridonium bromide solution:
● Λ vs. $\sqrt{c}$ curve and ○ $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curve.

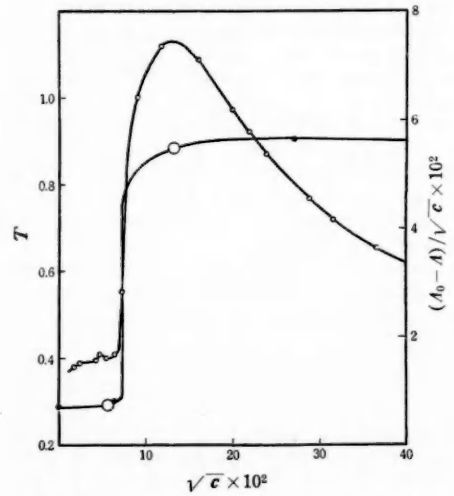

Fig. 2. Comparison of transport number diagram with $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagram for tetradecyl ammonium chloride:
• and ○ transport number, and
◦ $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagram.

of the maximum found by Hartley, as shown in Fig. 1.

Hartley made the following explanation for the occurrence of the maximum. At the concentration of surfactant near usual *C.M.C.*, the gegenions fixed on micelles are dissociated by applying high electric field; therefore, the gegenions and multicharged micelles come to contribute to the electroconductivity, and this contribution increases anomalously. At a more concentrated region, the fixed gegenions can not dissociate even in such a strong field; then the conductivity begins to fall again.

The C_{max} may be considered to show the concentration at which the fixation of gegenions on micellar surface is completed.

Furthermore, the data of transport number support this consideration. Ralston[4] found that the curve of transport number against the square root of normality shows a breaking point at a low concentration corresponding to the *C.M.C.*, and rises sharply to an anomalously high value with the increase of concentration, and then levels off. The concentration at which the value of transport number attains this anomalously high value is in good agreement with C_{max}, as shown in Fig. 2. After attaining this value, the transport number keeps a constant level in ordinary concentration, which means that the electrical charge of micelle becomes constant if the equal size of micelle is assumed. That is, the fixation of gegenions on micellar surface may be considered to be completed at this point.

Table I shows the correspondence between this concentration and C_{max} of some alkyl amine hydrochlorides.

On the other hand, it may be supposed that C_{min} indicates the concentration at which the fixation of gegenions begins.

4) A. W. Ralston, C. W. Hoerr and E. J. Hoffman, *J. Am. Chem. Soc.*, **64**, 97 (1942).

TABLE II

C_{min}, C_{max}, H_{min}, H_{max} AND B VALUES OF OCTADECYL PYRIDONIUM SALTS WITH REFERENCE TO THEIR GEGENIONS

Substance		C_{min}	C_{max}	H_{min}	H_{max}	B
$C_{18}H_{37}$–N	NO_3	(1.14)	0.42	(1.20)	19.6	4300
	Cl	0.24	1.09	0.30	11.0	1530
	IO_3	0.48	4.90	−3.85	2.80	374

The steepest region between C_{min} and C_{max} will be considered the region in which the gegenions are fixed. By this assumption, it is reasonable to suppose that the great change in electroconductivity takes place at the region between C_{min} and C_{max}.

The meaning of H_{max}

To consider the meaning of H_{max}, the effect of gegenions on the maximum point is very suggestive. It was recognized by Hartley[3] and others[5-7] that the gegenions of ionic surfactant play an important role in the formation of micelles and that the *C.M.C.* of surfactant depends on the degree of hydration of gegenions.

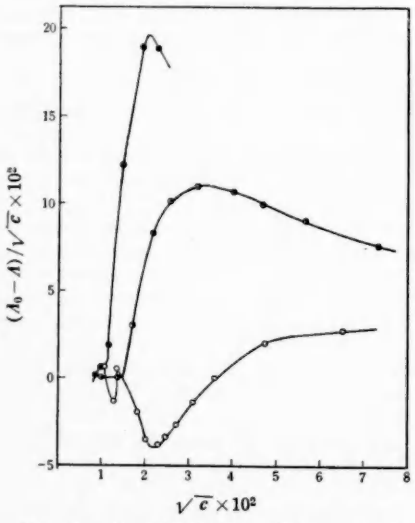

Fig. 3. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curves for the aqueous solutions of octadecyl pyridonium ● nitrate, ◑ chloride and ○ iodate at 25°C.

To see the relation between the degree of hydration of gegenions and C_{max}, H_{max}, etc., our method was applied to octadecyl pyridonium nitrate, chloride and iodate, and the results obtained are illustrated in Fig. 3 and Table II, in which it must be noted that there is good correspondence between C_{max} or H_{max} and lyotropic series of gegenions as below:

(a) The lyotropic number increases in the order:

$$\underset{5.2}{IO_3} < \underset{10.0}{Cl} < \underset{11.6}{NO_3}$$

(b) The value of C_{max} decreases in the order:

$$\underset{4.9}{IO_3} > \underset{1.09}{Cl} > \underset{0.42}{NO_3}$$

(c) The value of H_{max} increases in the order:

$$\underset{2.8}{IO_3} < \underset{11.0}{Cl} < \underset{19.6}{NO_3}$$

The adsorption (fixation) of gegenions on the surface of micelles is important for the explanation of the above relations. Considering the work of Wo. Ostwald[8] and Y. Osaka[9] on the adsorption of salts on charcoal, we have reached the following conclusion.

(a) The larger the degree of hydration of ion, the higher the concentration, at which the adsorption attains saturation.

(b) The higher the degree of hydration, the larger the quantity of adsorbed ions at saturation.

It may be considered from the relation (a) that the adsorption of gegenions on the micelle surface is saturated as in the above order.

On the other hand, it may be assumed that H_{max} depends on the quantity of ions adsorbed at saturation. If the quantity of gegenions adsorbed on micelle at saturation is large, the variation of electroconductivity also becomes large; then, H_{max} becomes large.

5) P. F. Grieger and C. A. Kraus, ibid., **70**, 3803 (1948).
6) G. L. Brown, P. F. Grieger and C. A. Kraus, ibid., **71**, 95 (1949).
7) K. Meguro, T. Kondo et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1236 (1956).
8) Wo. Ostwald, *Kolloid-Z.*, **87**, 128 (1939).
9) Y. Osaka, *J. Tokyo. Chem. Soc.*, **37**, 241 (1916).
10) Wo. Pauli and L. Sternbach, *Kolloid-Z.*, **84**, 291 (1938).

A new concept for the mechanism of micelle formation

In the above considerations, some doubts still remain as to whether the micelle formation precedes the fixation of gegenions or fixation of gegenions and micelle formation occur simultaneouly; that is, the fixation causes the micelle formation.

Some suggestion on this problem can be obtained in the correspondence between surfactant solution and polyelectrolyte solution.

Pauli,[10] Seiyama[11] and Takahashi[12] found the following Λ vs. $\sqrt{c}$ diagram for sodium alginate solution (Fig. 4.), which is very similar to the one of surfactant solution.

Furthermore, Koizumi and Mataga[13] found the disappearance of fluorescence of Rhodamine 6G by addition of a small amount of potassium polyvinyl sulfate: they also found the recovering of fluorescence in concentrated solution of this polyelectrolyte. The same phenomenon can be found in the case of sodium dodecyl sulfate and Rhodamine 6G system; that is, when the concentration of surfactant is lower than its *C.M.C.*, the fluorescence disappears, while it recovers when the concentration is over the *C.M.C.*

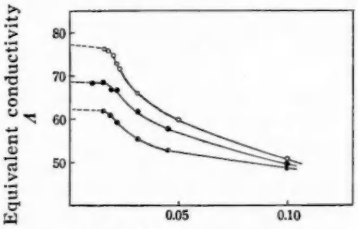

Fig. 4. Λ vs. $\sqrt{c}$ diagram for sodium alginate solution. (taken from Takahashi).

Degree of polymerization of Na alginate ○ 11 ● 35 ◐ 97

If we assume that a molecule of polyelectrolyte corresponds to a micelle of surfactant it will be reasonable to assume the fall of Λ in Λ vs. $\sqrt{c}$ diagram and of the recovering of fluorescence of dye would not be caused by the formation of micelles but by the fact that the number of micelles reaches some definite amount.

According to the theory of Osawa and Kagawa[14], many phenomena for polyelectrolyte solution will be explained by the fixation of gegenions on polyelectrolyte ion; then the dropping of Λ and the recovering of fluorescence in surfactant solution will also be explained as follows;

(1) Owing to the amphipathic properties of surfactant, loose micelles exist in more dilute solution than usual *C.M.C.*.

(2) When the concentration of these loose micelles reaches a definite value, the gegenions are fixed on them; then the charges on micellar surface decrease, decreasing the repulsion among surfactant ions which form micelles, and the micelles become compact. That is to say, the usual *C.M.C.* indicates the concentration at which the compact micelles begin to form.

It should be considered that the micelles of non-ionic surfactants are formed on account of their amphipathic properties; therefore, in this case only the loose micelles can be produced. This fact will be ascertained by the obscurity of critical phenomena in nonionic surfactant solution.

If we consider two types (loose and compact) of micelle, it is necessary to take into account the following facts regarding the discussion of effects on critical phenomena of surfactant solution.

(I) The effects which alter the concentration where the compact micelles appear.

(II) The effects which alter the ability of forming micelles.

The solvent effect and the salt effect on critical phenomena will be ascribed mainly to the effect mentioned in I, but the effect mentioned in II is not well known.

We found the effect which will be regarded as the one mentioned in II in the system of non-ionic and ionic surfactant mixture.

The effect of the addition of polyoxyethylene dodecyl ether on the conductivity of sodium dodecyl sulfate solution was measured.[15] As a result, the following Λ vs. $\sqrt{c}$ diagram was obtained (Fig. 5), which is charaterized by the facts that the breaking point of sodium dodecyl sulfate corresponding to its *C.M.C.* in the usual sense becomes less pronounced with

11) T. Seiyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **53**, 122 (1950).
12) T. Takahashi, K. Kimoto and Y. Takano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 292 (1951).
13) M. Koizumi and N. Mataga, ibid., **75**, 273 (1954).
14) F. Osawa, N. Imai and I. Kagawa, *J. Polymer Sci.*, **13**. 93 (1954).
15) O. Yoda, K. Meguro, T. Kondo and T. Ino, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 905 (1956).

increasing concentration of the non-ionic surfactant and almost disappears at 10^{-2} M of non-ionic surfactant without a shift of the breaking point toward either side of concentration. This phenomenon is really new, and usually the additions of salt, solvent and solubilizate are accompanied by shifts of the breaking point.

The $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagram based on the same data is shown in Fig. 6, in which it is noticed that the C_{min} gradually disappears without a shift as the amount of added non-ionic surfactant increases, and that the H_{max} becomes lower and the slope turns less steep with increasing concentration of non-ionic surfactant. Because H_{max} is proportional to the amount of gegenions adsorbed on micelle surface, and because C_{min} shows the concentration at which the compact micelle begins to form by the fixation of gegenions, we can consider that the addition of non-ionic surfactant prevents the formation of compact micelles. This consideration will be supported by the following experiment.

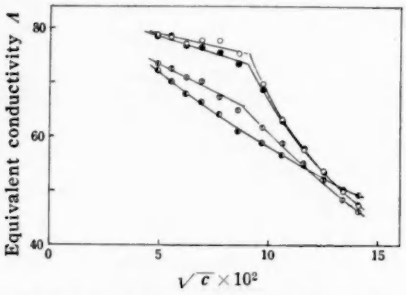

Fig. 5. Λ vs. $\sqrt{c}$ curves for sodium dodecyl sulfate in the aqueous solutions of polyoxyethylene dodecyl alcohol ether:
○ in water, ● 10^{-4}, ① 10^{-3} and ◐ 10^{-2} mole/l.

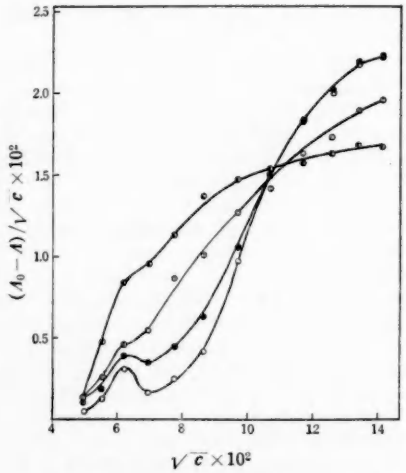

Fig. 6. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curves for sodium dodecyl sulfate in the aqueous solution of polyoxyethylene dodecyl alcohol ether:
○ in water, 10^{-4}, ① 10^{-3} and ◐ 10^{-2} mole/l.

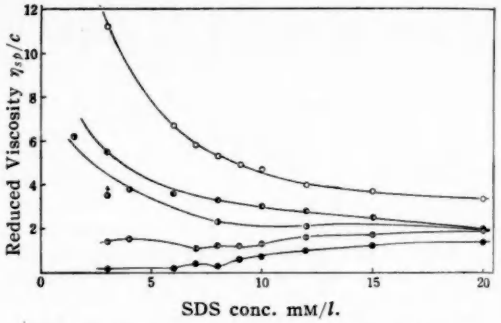

Fig. 7. η_{sp}/c vs. c diagram for sodium dodecyl sulfate in the aqueous solution of polyoxyethylene dodecyl alcohol ether:
● in water, ① 1×10^{-3}, ◑ 2.5×10^{-3}, ◐ 5×10^{-3} and ○ 1×10^{-2} mole/l.

Sata and Tyuzyo[16] found the minimum of η_{sp}/c in the diagram of η_{sp}/c vs. c for the solution of ionic surfactant. We found that the small addition of non-ionic surfactant cancels this minimum, and the curve of η_{sp}/c vs. c approaches to that of polyelectrolyte solution rather than that of surfactant solution (Fig. 7). This fact can be considered that the non-ionic surfactant (molecular or loose micellar) adsorbs ionic surfactant on its lyophobic groups and therefore the micelle formation of ionic surfactant is prevented.

It seems necessary to discuss the various effects on critical phenomena from the two standpoints mentioned above, and these considerations are very useful to obtain the real feature of various effects.

In above explanation our discussion was mainly focused on the compact micelles. Now we should consider the formation of loose micelles, but it is impossible to consider its formation because of the lack of exact data of electroconductivity in very dilute surfactant solution.

Nedzu Chemical Laboratory, Musashi University, Nerima, Tokyo

16) N. Sata and K. Tyuzyo, This Bulletin, **26**, 177 (1953).

Colloid Chemical Studies on Starching Materials. II. Intrinsic Viscosity of Polyvinyl Alcohol in Soap Solutions

By Masayuki NAKAGAKI and Hiroko NISHIBAYASHI*

(Received December 9, 1957)

In the preceding paper[1], the structural viscosity of aqueous solutions of polyvinyl alcohol was studied. In this paper, some results will be reported on the viscometric behavior of polyvinyl alcohol in soap solutions. This study has been made in order to see whether there exists any interaction between polyvinyl alcohol and soap. The interaction of non-ionic high polymer molecules and anionic detergent molecules will be of some interest in the field of both polymer and surface chemistry. It may, further, be of some interest in the field of textile industry, since experiments of this kind will give some fundamental information on the process of removing starching material from the surface of textile fibers.

Experimental

Polyvinyl alcohol.—Two materials provided by Nippon Gosei Kagaku Kogyo K. K., Gohsenol NM-14 and GM-14, were used[2]. The degree of polymerization of both NM and GM is about 1400. The degree of saponification of NM is 99~100%, while that of GM is 90±2%. Two grams of the polymer was dissolved in water by heating at 90°C for 15 min. After being cooled, it was transferred into a volumetric flask and made up to 100 cc. in a thermostat at 40°C. This solution, to be used after volumetric dilution, was prepared on the day when measurements were made, because the viscosity would slightly increase day by day. The method of dissolving the polymer affects the viscosity of the solution as discussed in the preceding paper. Heating for 15 min. is not long enough so that the molecules are probably not fully extended in the solution. This is one of the reasons for the increase of viscosity by aging. The above described method was, however, adopted considering the practical method of preparation of starching solution. Water used throughout the experiments was for the electric conductivity measurement.

Soap.—Sodium laurate was used. Lauric acid (m. p., 44.95°C) was neutralized with sodium hydroxide (extra pure reagent grade, rods) in conductivity water at 90°C. Sodium hydroxide was always used in 2% excess, in order to prevent the hydrolysis of the soap.

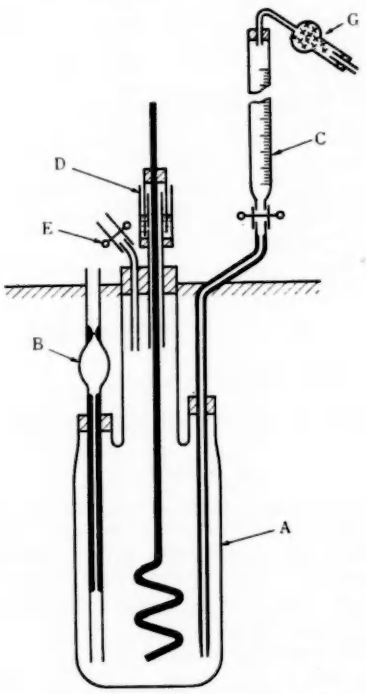

Fig. 1. Viscometer

Viscometer.—A viscometer illustrated in Fig. 1 was used. This is a flask of cylindrical shape (A) with three openings, equipped with a viscometer (B), a burette (C) with a soda lime tube (G), a stirrer (D) and a glass and rubber tubing closed with a pinchcock (E). In the flask (A), 50 cc. of soap solution containing or not containing polyvinyl alcohol was placed and a solution of the same soap concentration and of a different polyvinyl alcohol concentration was added from the burette. After being stirred with D, viscosity was measured with B, with E opened during the measurement. Thus the viscosity of the solution of various concentration of polyvinyl alcohol in a certain soap concentration was measured. The time for distilled water to flow down the viscometer was measured in advance for each

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1) M. Nakagaki and A. Shimazaki, This Bulletin, **29**, 60 (1956).

2) Gohsenol contains a small amount (probably less than 1%) of sodium acetate, but the writers do not believe this affects the results essentially.

amount of water in the flask, on the basis of which the viscosity of the solution relative to distilled water was calculated. Dividing this by the relative viscosity of the soap solution of the same concentration, the viscosity of the solution relative to the soap solution as the solvent was calculated and designated by η_r. All experiments were made in a thermostat at 40°C.

Results and Discussions

Treatment of the Experimental Values.—On treating the experimental values there are several points to be considered. At first, the effect of velocity gradient should be taken into account. Solutions of Gohsenol usually show structural viscosity. The apparent viscosity is, then, a function of the rate of flow, Q(cc./sec.), as shown in the preceding paper[1]. The quantity Q or $1/Q$ is, however, not very adequate to compare the effect of velocity gradient in two capillaries of different radius. On the basis of Poiseuille's law, the largest velocity gradient, G_m, that is the velocity gradient on the wall of the capillary, is

$$G_m = (4/\pi a^3)Q \tag{1}$$

The average velocity gradient, G, defined by

$$\bar{G} = \int_0^a G(r)2\pi r\,\mathrm{d}r/\pi a^2 \tag{2}$$

is related to the largest velocity gradient by

$$G = (2/3)G_m \tag{3}$$

where a is the radius of the capillary and r is the distance between the axis of the capillary and the point where the velocity gradient is being considered. Either G_m or G may be used to discuss the effect of velocity gradient.

In the present experiments, the value of G_m was in the range between 1000 to 4000 (sec.$^{-1}$), which corresponds to the range of $(1/Q)$-value between 8 and 35 for the viscometer used in the preceding paper. Because of this low value of $1/Q$, it is clear according to the results of the preceding paper[1] that the viscosity data in the present paper is very close to the value of η_N, that is the viscosity value extrapolated to zero of $1/Q$. Therefore, the effect of the velocity gradient may be neglected in the present experiments.

The viscometer used in this experiment is suitable to study the concentration dependence of the viscosity. However, the data should be extrapolated to zero concentration in order to obtain the value of the intrinsic viscosity. There are two well known equations for this purpose, that is Huggins' equation,

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2c \tag{4}$$

and Staudinger's equation,

$$\ln \eta_r/c = [\eta] - k_2[\eta]^2c \tag{5}$$

where c is the concentration of polymer. It was pointed out by Heller[3] that the simultaneous use of these two equations can appreciably reduce the arbitrariness in the extrapolation. For this purpose, both η_{sp}/c and $\ln \eta_r/c$ are expressed by $f(c)$ and plotted on the same figure. Three typical pairs of curves thus obtained are shown in Fig. 2. The upper curve of a pair corresponds to η_{sp}/c and the lower to $\ln \eta_r/c$.

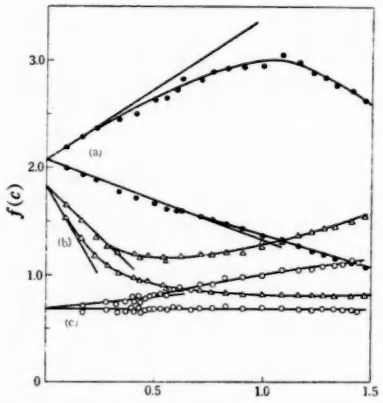

Fig. 2. Three types of $f(c)$-plot.
(a) Gohsenol NM in 0.1 N soap
(b) Gohsenol GM in 0.025 N soap
(c) Gohsenol NM in water

Experimental Results.—The value of the intrinsic viscosity, $[\eta]$, and the limiting slope of $f(c)$ curves, $k_1[\eta]^2$ and $k_2[\eta]^2$, are shown in Table I. In this experiment, the concentration of soap, c_s, shown in the first column is kept constant and the concentration of polymer, c, was changed.

At first, experiments were made using Gohsenol NM. As shown in Table I, the intrinsic viscosity increases when the soap concentration exceeds 0.025 N, which is close to the critical micelle concentration of sodium laurate[4]. This agrees with the experimental observation by Saito[5] that the viscosity of polyvinyl

3) W. Heller, *J. Colloid Sci.*, **9**, 547 (1954).
4) On the critical micelle concentration of sodium laurate, many investigators gave values between 0.02 and 0.028 N, the most probable value being 0.0255 N.
5) S. Saito, *Kolloid-Z.*, **133**, 12 (1953).

alcohol solution increases by addition of sodium oleate or some other detergents. The detailed behavior of the system in soap solutions near the critical micelle concentration will, therefore, be of some interest. This was studied by using Gohsenol GM, which is a little easier to handle than NM.

TABLE I
CONSTANTS IN HUGGINS' AND STAUDINGER'S EQUATIONS

Soap concn.	Gohsenol NM			Gohsenol GM		
c_s(N)	$[\eta]$	$k_1[\eta]^2$	$k_2[\eta]^2$	$[\eta]$	$k_1[\eta]^2$	$k_2[\eta]^2$
0	0.68	0.22	0	0.71	0.24	0
0.005	0.70	0.27	0	—	—	—
0.01	0.68	0.22	0	0.73	0.27	0
0.02	—	—	—	0.71	0.26	0
0.025	0.73	0.27	0	1.16	−0.62	1.24
0.03	—	—	—	1.82	−1.90	3.40
0.04	—	—	—	2.24	−0.84	3.13
0.05	1.62	0.55	0.76	1.98	0.99	0.94
0.1	1.80	0.88	0.69	2.07	1.33	0.84
0.15	1.76	0.81	0.71	—	—	—

The results are also shown in Table I. In this concentration range, the intrinsic viscosity has a maximum.

In a soap solution of low concentration, $\ln \eta_r/c$ is almost constant in the range of the polymer concentration studied here, as an example of the case is shown in Fig. 2 (c). Therefore, $k_2[\eta]^2$ is equal to zero. In a soap solution of high concentration, η_{sp}/c increases and $\ln \eta_r/c$ decreases with polymer concentration, c, at the range of low values of c. An example is shown in Fig. 2 by curve a. In this case, both $k_1[\eta]^2$ and $k_2[\eta]^2$ are positive. In a soap solution of intermediate concentration, both η_{sp}/c and $\ln \eta_r/c$ increases when the concentration of polymer approaches to zero. An example of this type of curves is shown by curve b in Fig. 2. In this case, $k_1[\eta]^2$ is negative and $k_2[\eta]^2$ is positive.

Examination of k_1 and k_2.—The values of k_1 and k_2 were calculated from data given in Table I and shown in Fig. 3, together with the value of $[\eta]$, as a function of the soap concentration c_s. The short vertical lines at c_s=0.025 N show the critical micelle concentration of the soap. At about this soap concentration, the intrinsic viscosity and k_2 increase while k_1 decreases abruptly. The curve of $[\eta]$ and k_2 has a maximum and the curve of k_1 has a minimum.

The relation between k_1 and k_2 is shown in Fig. 4. The straight line shows the well known relation,

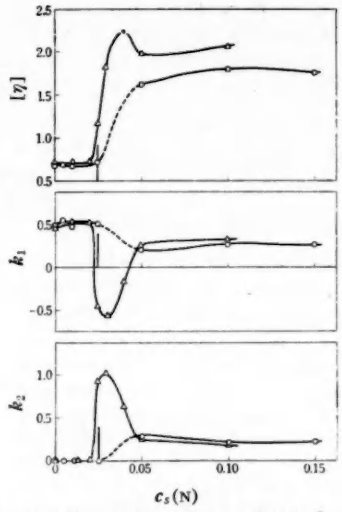

Fig. 3. The c_s dependence of $[\eta]$, k_1 and k_2. ○ Gohsenol NM; △ Gohsenol GM.

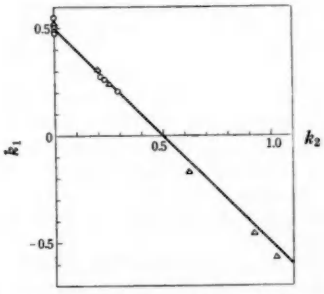

Fig. 4. Relation between k_1 and k_2.

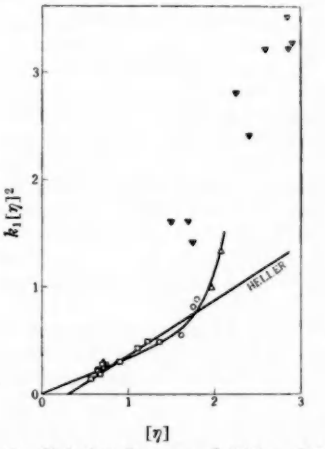

Fig. 5. Relation between $k_1[\eta]^2$ and $[\eta]$.
○ and △: Gohsenol
□ and ▽: Polystyrene

$$k_1 + k_2 = 0.5 \quad (6)$$

which had been pointed out by Ewart[6]. Fig. 4 shows that this relation can be extended to the negative values of k_1. This is a natural consequence because Ewart's relation can be derived mathematically from Eqs. 4 and 5.

The relation between $k_1[\eta]^2$ and $[\eta]$ is shown in Fig. 5. Eirich and Riseman[7] proposed an empirical relation,

$$k_1[\eta]^2 = \alpha + \sigma[\eta] \quad (7)$$

where α and σ are constants. Using data by Streeter and Boyer[8] on polystyrene ($\bar{M}_w = 3.7 \times 10^5$) in various organic solvents, values $\sigma = 0.50_7$ and $\alpha = -0.14_6$ were obtained by Heller[3]. This relation is shown in Fig. 5 by a straight line and individual data by □. On the other hand, the present data were plotted for Gohsenol NM by ○ and GM by △, except for three points of negative k_1 values. According to these data, $k_1[\eta]^2$ increases more rapidly than the straight line by Heller at large $[\eta]$ values. This is, however, not strange if we refer to the values given by Cragg[9], which are based on data by Bawn et al. on polystyrene ($M = 1.6 \times 10^6$) in various organic solvents and shown in Fig. 5 by ▽. Therefore, the relation between $k_1[\eta]^2$ and $[\eta]$ of polyvinyl alcohol-soap-water system studied in this paper follows the same tendency as that of polystyrene in organic solvents, except the case for which k_1 is negative.

Interaction between Polyvinyl Alcohol and Soap.—On the basis of the experimental observations described above, polyvinyl alcohol is being dissolved in soap solution in three different states depending on the concentration of soap.

(1) In a soap solution at the concentration lower than its critical micelle concentration, polyvinyl alcohol behaves as it does in water. It is therefore concluded that the effect of soap is negligible at this low concentration. Here, $[\eta]$ is small, k_1 nearly equal to 0.5 and k_2 is nearly equal to zero. This is the usual behavior of polyvinyl alcohol in water, or more generally, of nonionic polymer in a rather poor solvent.

(2) In a soap solution near the critical micelle concentration $[\eta]$ is large, k_1 is negative and k_2 is larger than 0.5. The negative value of k_1, or a rapid increase of η_{sp}/c with decreasing polymer concentration, is usually observed on aqueous solutions of polyelectrolytes. In this range of soap concentration, therefore, polyvinyl alcohol molecules are supposed to be combined with soap molecules, and to behave like polyelectrolyte molecules because of the electrical charges due to the soap ions. The combination of polyvinyl alcohol and soap occurs near the critical micelle concentration of the soap, but the formation of micelle does not seem to be very important to this combination, because at the critical micelle concentration (0.025 N) the intrinsic viscosity of Gohsenol NM is still low while that of Gohsenol GM is already large. This may suggest that the combination of soap with polyvinyl alcohol is due to the aggregation of the hydrophobic part of the soap molecule with the hydrophobic part of the polymer molecule. This will explain the fact that the combination occurs near the critical micelle concentration, because the micelle formation of soap is also due to the aggregation of hydrophobic part of soap molecules. This will, further, explain that Gohsenol GM combines with soap at lower soap concentration than Gohsenol NM does, because GM retains about 10% of acetyl groups so that it is more hydrophobic than NM, the latter being saponified completely.

(3) In a soap solution of high concentration, $[\eta]$ is large and both k_1 and k_2 are positive. This is the usual behavior of nonionic polymer in a good solvent. This will mean that the electric charges of soap molecules combined with the polymer are shielded completely by the ion atmosphere of the counter ion (sodium ion) at this high soap concentration, so that the polymer behaves like a nonionic polymer. The high value of the intrinsic viscosity may be due to the following several reasons. a) The carboxyl group of soap combined with the polymer adds hydrophilic property. A polymer molecule is usually the more extended, the higher the affinity of the polymer to solvent. b) As far as the intermolecular interaction of polymer molecules are concerned, it has been assumed that the electric charge of soap combined with the polymer is completely shielded by counter ions. However, the shielding is probably not perfect inside the molecule. The electric repulsion between segments in a polymer molecule will extend the polymer. c) The soap

6) R. H. Ewart, *Advances in Colloid Sci.*, **2**, 211 (1946).
7) F. Eirich and J. Riseman, *J. Polymer Sci.*, **4**, 417 (1949).
8) D. J. Streeter and R. F. Boyer, *Ind. Eng. Chem.*, **43**, 1790 (1951)
9) L. H. Cragg, *Chem. & Ind.*, **1952**, 623.

molecules combined with the polymer will occupy its own volume. This will make the polymer molecule expanded. d) By the combination with soap molecules, polymer molecules become stiff and lose flexibility to some extent. This will also result the extension of the polymer molecules. The extension of polymer molecules by these reasons will increase the intrinsic viscosity.

Summary

The concentration dependence of the viscosity of polyvinyl alcohol in solutions of constant soap concentration is studied. At the soap concentration lower than its critical micelle concentration, the effect of soap on the viscosity of polyvinyl alcohol is very little. At the soap concentration near the critical micelle concentration, soap molecules are combined with the polymer, the latter behaving like a polyelectrolyte. At high soap concentration, the polymer behaves like a non-ionic polymer in a very good solvent.

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Solvent Effects on the Fluorescence of Some π-Electron Systems Naphthylamine and Naphthol

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Heretofore, in a series of investigations[1-5], we have examined some aspects of solvent effects on the fluorescence of π-electron systems, especially concerning the hydrogen bonding effect.

a) Firstly, a general formula for the difference of solvent shifts of fluorescence and absorption spectra in the approximation of long range dipolar interaction was derived using Ooshika's theory[6] of light absorption in solution. Measurements of fluorescence and absorption spectra of some naphthalene derivatives in various organic solvents were undertaken, and the experimental data were analyzed by the theoretical formula. The formula reproduces the experimental data satisfactorily, and from this fact it was concluded that the most predominant factor which determines the difference of solvent shifts of fluorescence and absorption spectra of these molecules is the interaction energy between solute and solvent molecules due to orientation polarization. The incremental values of dipole moments in the excited state were estimated, and those for α, β-naphthols and β-naphthyl methylether were interpreted as due to the increase of electron migration from the substituent in the excited state.

b) Secondly, the question whether a new and different equilibrium of the hydrogen bond formation is reached during the lifetime of the excited state, was examined using the solutions of α- and β-naphthol as fluorescers and proton donors in non-polar solvent mixed with various proton acceptors.

By quantitative treatment of the experimental results, it was confirmed that β-naphthol in the excited state has a greater tendency toward hydrogen bonding, a new equilibrium being attained during its lifetime.

c) Thirdly, the effect of hydrogen bond formation on the fluorescence yield of the mother substance was investigated, from which some facts of the mechanism of non-radiative degradation of excited state

1) N. Mataga, Y. Kaifu and M. Koizumi, This Bulletin, **28**, 690 (1955); **29**, 465 (1956).
2) N. Mataga, Y. Kaifu and M. Koizumi, *Nature*, **175**, 731 (1955); This Bulletin, **29**, 116 (1955).
3) N. Mataga and S. Tsuno, ibid., **30**, 368 (1957).
4) N. Mataga and S. Tsuno, *Naturwiss.*, **44**, 304 (1957).
5) N. Mataga and S. Tsuno, This Bulletin, **30**, 711 (1957).
6) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954).

due to inter- or intra-molecular processes, were obtained. The role of non-bonding electrons in the inner quenching of some nitrogen heterocycles, and the effect of π-electronic state on the fluorescence quenching caused by the near-by existence of halogen atoms, were studied. The cause of the inner quenching in nitrogen heterocycles was attributed to the n-π interaction in the excited state. The difference between quinoline and acridine in their fluorescence quenching caused by the existence of a halogen atom was ascribed to the different emitting states in these molecules (^1L_b in quinoline, ^1L_a in acridine), and some considerations were made assuming a close similarity of the electronic states of nitrogen heterocycles to those of the parent hydrocarbons. This assumption has been confirmed by some quantum mechanical calculations[7,8].

Fluorescence quenching caused by the hydrogen bond formation between nitrogen heterocycles as proton acceptors and fluorescers, and proton donors such as phenol, naphthol, aniline and pyrrole which are capable of making hydrogen bond intimately related with π-electron systems, was investigated, and interpreted as due to the delocalization of π-electrons through the hydrogen bond, in the excited state.

In the present paper, we shall report other examples of the solvent effect on fluorescence spectra, the shift of the hydrogen bonding equilibrium in the excited state, and the fluorescence quenching due to hydrogen bond formation, in which naphthylamine and naphthol are used as fluorescers and proton donors, and pyridine and acetic acid esters as proton acceptors.

Experimental

Apparatus:—Absorption spectra were measured with a Beckman Spectrophotometer model DU. Fluorescence spectra were photographed with small-type glass prism spectrograph. The fluorometer was the same as described previously[2]. Filters used for naphthol are the same as before[2], and for naphthylamine, they are as follows: for exciting light, Matsuda color filter UV-DI which takes out 365 mμ line of mercury lamp, and for fluorescent light, the yellow filter, attached to Beckman photometer for fluorescence analysis, the transmittance of which is nearly 90 % in all the visible spectral region longer than 410 mμ, were used.

Reagent:—β-Naphthol and β-naphthylmethyl ether were the same samples as used before[2]. Chemical-pure grade α- and β-naphthylamine were purified by repeated recrystallization from ligroin. Extra-pure grade *N*, *N*-dimethyl-β-naphthylamine was purified by repeated distillation in vacuo. Acetic acid esters[2] and trichloroacetic acid[3] were the same samples as described previously. Extra-pure grade pyridine was dried over sodium hydroxide and distilled carefully Benzene was the same as described elsewhere[5].

7) N. Mataga, to be published in this Bulletin.
8) N. Mataga, to be published in this Bulletin.

Experimental Results and Discussion

When acetic acid esters are added to the solution of naphthylamine in benzene, the features of phenomena are similar to the case of naphthol. When hydrogen bonded with acetic acid esters, enhancement of fluorescence intensity compared with free molecules is observed, and the excited molecules have greater tendency to form hydrogen bonds, a new equilibrium being reached during the lifetime of the excited state.

When hydrogen bonded with pyridine, however, fluorescence is almost completely quenched, and it is also the case for naphthol. This quenching phenomenon is similar to the previously reported one[5] of non-radiative degradation caused by hydrogen bonding, but the fluorescer and the quencher have exchanged their roles as proton acceptor and donor, with each other.

A. Changes of Absorption Spectrum Caused by Hydrogen Bonding.—Absorption spectra are somewhat strengthened and shifted to red by hydrogen bonding. Some examples of these changes are shown

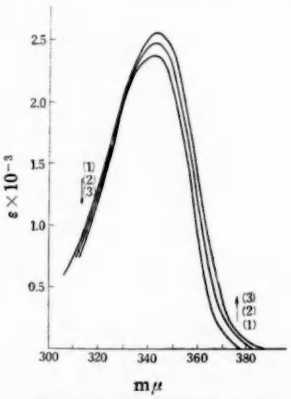

Fig. 1. Change of absorption spectrum of β-naphthylamine in benzene produced by added pyridine.
Concentration of pyridine: (1) 0, (2) 4.96×10^{-1} mole/l., (3) 1.24 mole/l.

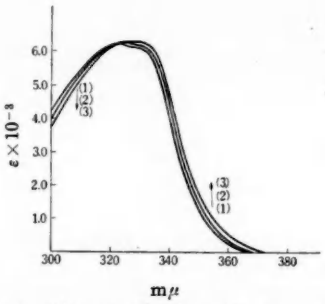

Fig. 2. Change of absorption spectrum of α-naphthylamine in benzene produced by added butyl acetate.
Concentration of butyl acetate: (1) 0, (2) 1.23 mole/l., (3) 2.76 mole/l.

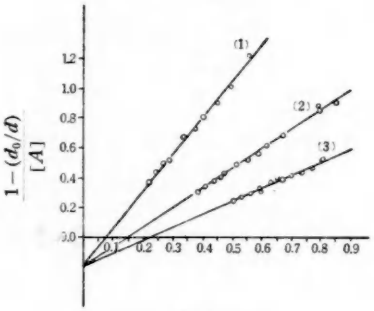

Fig. 3. $\frac{1-(d_0/d)}{[A]}$ vs. (d_0/d) relation for β-naphthylamine-pyridine-benzene system at several wave lengths: (1) 370 mμ, (2) 365 mμ, (3) 362 mμ.

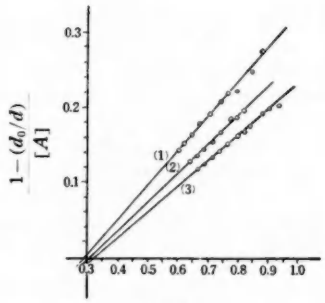

Fig. 4. $\frac{1-(d_0/d)}{[A]}$ vs. (d_0/d) relation for α-naphthylamine-butyl acetate-benzene system at several wave lengths: (1) 365mμ, (2) 354 mμ, (3) 352 mμ.

in Figs. 1 and 2. The change of optical density at a definite wave length is well reproduced by Eq. 1[3]

$$\frac{(1-d_0/d)}{[A]} = -K^{(g)} + (\varepsilon'/\varepsilon)\cdot K^{(g)}\cdot(d_0/d) \quad (1)$$

The equilibrium constants $K^{(g)}$'s of hydrogen bond formation obtained by means of this formula, at several wave lengths, nearly coincide with each other. Some examples of these analyses are shown in Figs. 3 and 4.

B. Change of Relative Fluorescence Intensity Caused by Addition of Proton Acceptor.—Some examples of the enhancement or quenching of fluorescence of β-naphthylamine in benzene caused by the addition of proton acceptors are shown in Fig. 5. The features of these changes are also the same in the case of α-naphthylamine and of β-naphthol. If we use for these cases the following Eqs. 2[3] and 3*,

$$\frac{1-(f_0/f_\infty)(d_\infty/d_0)}{[A]} = -K^{(e)} + \alpha(d_m/d_0)K^{(e)}(f_0/f_m) \quad (2)$$

$$(f_m/f_0)(d_0/d_m) = \frac{1}{1+K^{(e)}[A]} \quad (3)$$

the experimental results are well satisfied by these equations, and the equilibrium constants $K^{(e)}$'s of hydrogen bond formation in the excited state are evaluated**. Some examples of these analyses are shown in Figs. 6 and 7. The equilibrium constants $K^{(e)}$'s obtained in this way are remarkably large compared with those evaluated from absorption spectra, as shown in Table I.

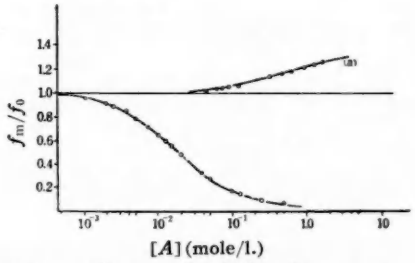

Fig. 5. Change of relative fluorescence intensity, f_m/f_0, of β-naphthylamine produced by added proton acceptors. Acceptors: (a) butyl acetate, (b) pyridine.

* Eq. 3 is obtained putting $\alpha=0$ in Eq. 2 which is the case for naphthylamines or naphthol-pyridine-benzene systems.

** Shifts of fluorescnce spectra of naphthylamines produced by the addition of acetic acid esters is very small in benzene, therefore we may be allowed to neglect the difference of phototube sensitivity for the fluorescence of free and hydrogen bonded naphthylamines.

TABLE I

acceptor	donor		
	α-naphthylamine	β-naphthylamine	β-naphthol
pyridine	$K^{(g)}_{285} : 0.15K^{(e)}_{286} : 53$	$K^{(g)}_{256} : 0.2\ K^{(e)}_{286} : 60$	$K^{(g)}_{287} : 41K^{(e)}_{287} : \sim 84$
$CH_3CO_2C_4H_9$	$K^{(g)}_{283} : 0.13K^{(e)}_{285} : \sim 1$	$K^{(g)}_{287} : 0.1\ K^{(e)}_{287} : \sim 1.8$	
$CH_3CO_2C_2H_5$	$K^{(g)}_{287} : 0.26K^{(e)}_{285} : \sim 1$	$K^{(g)}_{287} : \sim 0.26K^{(e)}_{287} : \sim 1.8$	

$K^{(g)}_T$ or $K^{(e)}_T$: T is the temperature (in unit of °K) at which the measurement was made.

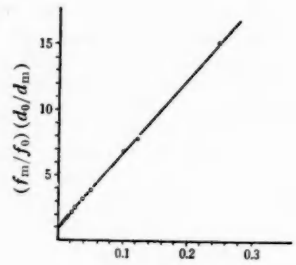

Fig. 6. $(f_0/f_m)(d_m/d_0)$ vs. $[A]$ relation for β-naphthylamine-pyridine-benzene system.

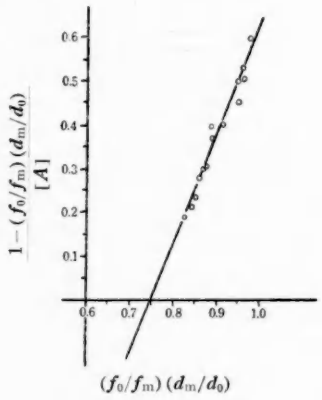

Fig. 7. $\frac{1-(f_0/f_m)(d_m/d_0)}{[A]}$ vs. $(f_0/f_m)(d_m/d_0)$ relation for β-naphthylamine-butyl acetate-benzene system.

When pyridine and acetic acid esters are added to the solutions of *N,N*-dimethyl-α-naphthylamine and β-naphthylmethyl ether in benzene, not even a slight change of fluorescence intensity has been observed throughout the whole range of acceptor concentration from ca. 10^{-3} to 1 mole/l.

Therefore, in the present case, the fluorescence quenching or enhancement may probably be wholly attributable to the hydrogen bond formation, and the equilibrium somewhat shifts to the side of association during the lifetime of the excited molecule. We can confirm further, whether the hydrogen bonding equilibrium in the excited state is really concerned with the fluorescence quenching or enhancement, as follows.

Let us examine the case in which the association equilibrium in the ground state is maintained in the excited state, the naphthylamines hydrogen-bonded with pyridine being completely non-fluorescent, and in which there is superposed the ordinary collisional quenching by pyridine. This is equivalent to assuming that, at the time of collision, pyridine affects specially the fluorescence of naphthylamines but not *N, N*-dimethylnaphthlamines. Then the deduction about the fluorescence intensity may be made according to the following scheme, were D and A are proton donor (fluorescer) and proton acceptor (quencher), respectively, and * denotes the excited state.

	rate or equilibrium
$D+A \rightleftarrows DA$	$K^{(g)}=[DA]/[D][A]$
$D+h\nu_a \rightarrow D^*$	$I_0\varepsilon[D]$
	$[D]=[D]_0/(1+K[A])$
$DA+h\nu_a \rightarrow DA^*$	$I_0\varepsilon'[DA]$
	$[DA]=K[A][D]_0/(1+K[A])$
$D^* \rightarrow D+h\nu_f$	$k_f[D^*]$
$D^* \rightarrow D$	$k_i[D^*]$
$DA^* \rightarrow DA$	$k_i'[DA^*]$
$D^*+A \rightarrow D+A$	$k_q[A][D^*]$

I_0: intensity of exciting light.

ε, ε': extinction coefficients of D and DA, respectively, at the wave length of exciting light.

By means of this scheme, the following formula for the relative fluorescence intensity is easily derived.

$$f_0/f_m = 1+(n_q+K^{(g)})[A]+n_qK^{(g)}[A]^2 \quad (4)$$

$$n_q = k_3/(k_f+k_i)$$

Now, let us assume that $K^{(e)}$ obtained by Eq. 3 is almost entirely contributed by n_q of Eq. 4, and plot f_0/f_m as a function of $[A]$.

As shown in Fig. 8, it is evident that the experimental results can not be reproduced by Eq. 4. Therefore, the possibility of the collisional quenching is rejected, and it is almost certain that the hydrogen

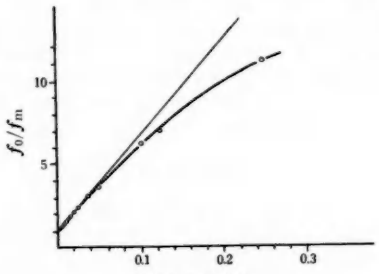

Fig. 8. f_0/f_m vs. [A] relation for β-naphthylamine-pyridine-benzene system.

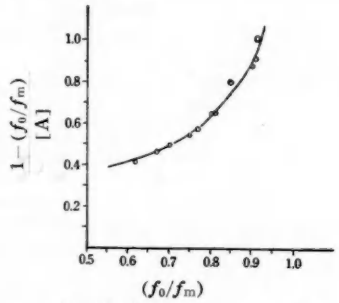

Fig. 9. $\frac{1-(f_0/f_m)}{[A]}$ vs. (f_0/f_m) relationf or β-naphtylamine-butyl acetate-benzene system.

bonding equilibrium shifts remarkably to the side of association during the lifetime of the excited state. For the case of enhancement of fluorescence intensity by acetic acid esters, the shift of equilibrium may be almost certain because Eq. 2 is satisfactorily reproduced by experimental results and the fluorescence of *N,N*-dimethyl-α-naphthylamine solution is not affected by the addition of the esters. If we use Eq. 5[3] which assumes that the equilibrium in the ground state is maintained in the course of fluorescence, instead of Eq. 2, we can see no agreement with experimental results, as shown in Fig. 9.

$$\frac{1-(f_0/f_m)}{[A]} = -K^{(g)} + \alpha(\varepsilon'/\varepsilon)K^{(g)}(f_0/f_m) \quad (5)$$

Further, let us examine, for this case, another possibility that the excited naphthylamine molecule is stabilized specifically by collision with acetic acid ester molecule, provoking the increase in fluorescence yield, though such an effect is very improbable in solution*. Now, let us assume the following scheme involving the equilibrium in the ground state, where the notations are the same as described above and s refers to the fluorescer molecule stabilized by collision.

	rate or equilibrium
$D+A \rightleftarrows DA$	$K^{(g)}=[DA]/[D][A]$
$D+h\nu_a \rightarrow D^*$	$I_0\varepsilon[D]$
$DA+h\nu_a \rightarrow DA^*$	$I_0\varepsilon'[DA]$
$D^* \rightarrow D+h\nu_f$	$k_f[D^*]$
$DA^* \rightarrow DA+h\nu_f'$	$k_f'[DA^*]$
$D^*+A \rightarrow D^{*s}+A$	$k_c[D^*][A]$
$D^{*s} \rightarrow D+h\nu_f$	$k_f^s[D^{*s}]$
$DA^* \rightarrow DA$	$k_i'[DA^*]$
$D^{*s} \rightarrow D$	$k_i^s[D^{*s}]$
$D^* \rightarrow D$	$k_i[D^*]$

According to this scheme, Eq. 6 is easily derived.

$$\frac{1-(f_0/f_m)}{[A]} = -(n_c+K^{(g)}+n_cK^{(g)}[A]) + \frac{(\Phi_0^s\varepsilon n_c+\Phi_0'\varepsilon'K^{(g)}+\Phi_0'\varepsilon'n_cK^{(g)}[A])}{\Phi_0\varepsilon} \times (f_0/f_m), \quad (6)$$

where

$$n_c=k_c/(k_f+k_i), \quad \Phi_0=k_f/(k_f+k_i),$$
$$\Phi_0'=k_f'/(k_f'+k_i'), \quad \Phi_0^s=k_f^s/(k_f^s+k_i^s)$$

Comparing this formula with Fig. 9, it is clear that the former is in essential disagreement with the latter. The possibility of collisional stabilization is thus completely neglected. The rather large difference of observed $K^{(g)}$ and $K^{(e)}$ of naphthylamines compared with that of naphthols may be partially comprehended as due to the difference of ionization potential of non-bonding electrons in the substituent (—OH: 10.95 eV., —NH_2: 9.41 eV.**,[9]). The degree of electron migration from the substituent and accordingly, also the difference of stabilization energy

* The increase in fluorescence yield of β-naphthylamine vapor in the presence of foreign gases was reported by Neporent[a]. Some aspects of his work on this molecule were confirmed by Curme and Rollefson[b] and detailed kinetical study was made by Boudart and Dubois[c].

a) B. S. Neporent, *Zhur. Fiz. Khim.*, **21**, 111 (1947); **24**, 1219 (1950). b) H. G. Curme and G. K. Rollefson, *J. Am. Chem. Soc.*, **74**, 28 (1952). c) M. Boudart and J. T. Dubois, *J. Chem. Phys.*, **23**, 223 (1955).

** These values are the ionization potentials of methanol and methylamine, respectively.

9) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

in the excited and ground state become larger, as the ionization potential of the substituent[10] becomes smaller.

Therefore, in the case of naphthylamines, the difference of the proton donating power in the excited and the ground state may be rather great, although the absolute value of proton donating power in the ground state may be small. In this respect, we have measured the solvent shifts of fluorescence and absorption spectra of naphthylamines in various organic solvents, and the results have been analyzed by Eq. 7[1,11]

$$-hc(\sigma_f^m-\sigma_a^m)\cong\text{Const.}+\left[\frac{2(D-1)}{2D+1}-\frac{2(n^2-1)}{2n^2+1}\right]\frac{(\vec{\mu}_e-\vec{\mu}_g)^2}{a^3} \quad (7)$$

where, σ_f^m and σ_a^m are wave numbers of peaks of fluorescence and absorption spectra, respectively, D and n dielectric constant and refractive index of the solvent, $\vec{\mu}_e$ and $\vec{\mu}_g$ dipole moment of solute molecule in the excited and the ground state, respectively and a is the cavity radius in Onsager's theory of reaction field.

Although we can not make a quantitative discussion because of the broadness of the spectra, it may be certain that the increments of dipole moments of naphthylamines in the excited state are not smaller than those of naphthols in the order of magnitude. In addition we refer to the fact that, Förster has estimated the difference of pK value in the excited and ground states of β-naphthylamine, in the case of the dissociation of the type, $-NH_2 \rightarrow -NH^- + H^+$, to be about 8 units[12], the excited state being very acidic compared with the ground state.

Now, as pointed out in the earlier part of this paragraph, the fluorescence quenching caused by hydrogen bonding with pyridine is analogous to the quenching phenomenon in the case of nitrogen heterocycles hydrogen bonded with phenols and aniline[5]. Accordingly, we may be allowed to say that the quenching in the present case also originates from the interaction between the π-electron systems via the hydrogen bond, in the excited state, although the fluorescer and quencher have reversed their roles as the proton acceptor and donor.

10) A. L. Sklar, ibid., **7**, 984 (1939); K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).
11) E. Lippert, *Z. Naturforsch.*, **109**, 541 (1955); *Z. physik. Chem.*, N. F., **6**, 125 (1956).
12) Th. Förster, *Z. Elektrochem.*, **54**, 531 (1950).

Summary

The enhancement or quenching of fluorescence intensity of naphthylamines and naphthol caused by hydrogen bonding with acetic acid esters or pyridine has been measured. By means of detailed analyses of the experimental results, it has been established that the shift of hydrogen bonding equilbrium toward the side of association is realized during the lifetime of excited state.

The cause of the shift has been interpreted on the basis of the theory of electron migration, and an evidence supporting the interpretation has been provided by measuring the solvent shift of fluorescence spectra. The mechanism of the fluorescence quenching has been discussed as due to the delocalization of π-electrons through the hydrogen bond.

The author expresses his gratitude to Professer S. Mizushima of Tokyo University for his encouragement. He is also grateful to Professor M. Koizumi of Tohoku University for his interest in this investigation. His thanks are especially due to Miss S. Tsuno for her experimental assistance throughout the present study. He is also thankful to Miss S. Wada for typewriting this paper.

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Fluorescence Quenching due to the Interactions between π-Electron Systems in the Excited State and Acid-Base Relation: Nitrogen Heterocycles, Naphthylamine and Naphthol in Aqueous and Alcoholic Solution

By Noboru MATAGA

(Received December 18, 1957)

In an earlier paper[1], we have reported the results of our investigation about the hydrogen bonding effect on the fluorescence of acridine, 3,6-diaminoacridine (DAA) and 3,6-bisdimethylaminoacridine (BDAA) in non-polar solvent mixed with proton donor such as phenol, naphthol, aniline and pyrrole. In these cases in which the hydrogen bond is capable of conjugating with the π-election system of proton donor, the fluorescence yields decrease as the result of hydrogen bonding formation in contrast to the case of donors such as benzylalcohol and β-phenylethylalcohol[2] in which the hydrogen bond is isolated by σ-bond from π-electron system, and with which hydrogen bonding leads to the enhancement of fluorescence yield. From the fact that no viscosity dependence of quenching has been observed, the possibility of the participation of diffusion-controlled dynamical process in the non-radiative degradation of excited state has been excluded. Moreover, we have also examined the case of naphthylamines and naphthol, hydrogen-bonded with pyridine where a remarkable fluorescence quenching has been observed[3]. Then the cause of the non-radiative degradation of excited state by means of hydrogen bonding has been attributed to the interaction between two π-electron systems via the hydrogen bond, viz., the delocalization of π-electrons through the hydrogen bond, especially in the excited state.

Hitherto, the ordinary experimental studies of the fluorescence quenching in the case of complex molecules, has been mainly carried out in aqueous or alcoholic solution, and the real nature of this phenomenon is not very clear up to now.

We have attempted to touch the real nature of the fluorescence quenching, in our series of investigation[1-7], mainly concerning with the case of hydrogen bond formation between fluorescer and quencher (or promoter) in non-polar solvent. The above mentioned case of fluorescence quenching due to the hydrogen bonding between the π-electron systems[1,3] may plausibly provide a more clear-cut example in relation to the mechanism of fluorescence quenching, and, in fact, it may be a new type of fluorescence quenching studied in a systematic manner. As an extention of our investigations, we have examined the behavior of the fluorescers and quenchers in aqueous and alcoholic solutions. We have found that, in this case, there exists some regularity in relation to the ability of a molecule as quencher or an approximate parallelism with the case of fluorescence quenching in non-polar solvent. This fact may probably suggest a somewhat analogous mechanism of quenching to the case of non-polar solvents, although, contrary to the case of the latter, the dynamical mechanism may be predominant in the present case. Moreover, the remarkable difference between aqueous and alcoholic solutions in this quenching phenomenon has become clear. In the present paper we shall report these facts with some discussions on the characterization of the quenchers and the influence of liquid structures of solvents on the fluorescence quenching.

Experimental

Apparatus: Absorption spectra were measured with Beckman Spectrophotometer model

1) N. Mataga and S. Tsuno, This Bulletin, **30**, 711 (1957).
2) N. Mataga and S. Tsuno, ibid., **30**, 368 (1957).
3) N. Mataga, to be published in this Bulletin.
4) N. Mataga, Y. Kaifu and M. Koizumi, *Nature*, **175**, 731 (1955); This Bulletin, **29**, 115 (1956).
5) N. Mataga and S. Tsuno, *Naturwiss.*, **44**, 304 (1957).
6) N. Mataga, to be published in this Bulletin.
7) N. Mataga, to be published in this Bulletin.

DU. Fluorometer was the same as described before[4]. A high pressure mercury lamp with appropriate filters was used as an exciting light source. Filters for quinoline, acridine[5] and DAA[1] are the same as used before. The filters used for β-naphthylmethyl ether and the ultraviolet fluorescence[9] of β-naphthol were the same as those of quinoline. For the blue fluorescence[9], the saturated solutions of nickel- and cobalt-sulfate and 0.2 g./l. potassium chromate solution each of which has 1 cm. thickness, were used as exciting light filters, taking out only 310 mμ line of mercury lamp, on the one hand, and yellow filter of Beckman photometer[3] was used for fluorescent light on the other hand. The filters used for β-naphthylamine and *N,N*-dimethyl-α-naphtylamine were the same as used before[3].

Reagent: All fluorescers and quenchers are the same samples as used before[1-5,8]. In order to control the pH of aqueous solution, citrate, phosphates and glycine were used. The reagents were of extra-pure grade, and used without further purification.

Experimental Results

In the following, the results for each fluorescer are described separately, and some of the data are collected in tables* in the latter part of this section. The concentrations of fluorescers are as follows; quinoline, β-naphthol, β-naphthylamine, β-naphylmethyl ether and *N,N*-dimethyl-α-naphthylamine, $\sim 10^{-4}$ mole/l.; acridine, 5×10^{-5} mole/l.; DAA, $\sim 10^{-5}$ mole/l.

In all cases described here, the absorption spectra showed no change caused by the addition of quenchers.

a) Quinoline: Only the quenching action of phenol and pyridine in aqueous solutions of appropriate pH values where the fluorescer exists exclusively as quinolinium ion, was examined quantitatively. The quenching curves in the case of phenol, are well reproduced by Stern-Volmer** equation, and the quenching constant becomes larger, with decrease in the pH value. The fluorescence is quenched also by pyrrole, almost completely disappearing at the quencher concentration, $\sim 10^{-1}$ mole/l. No quenching by pyridine, however, has been observed.

b) Acridine: The quenching actions of phenol, aniline pyrrole, and pyridine were examined mainly in aqueous solutions of various pH values. In the case of phenol, the dependence of quenching constant on the pH value is similar to the case of quinoline. Contrary to this, in the case of aniline, the quenching constant at pH 1 is the smallest. The quencher exists at this pH value, however, as anilinium cation. In contradistinction to the quenching in aqueous solution, the efficiency of phenol in ethanol solution is very poor, and, in practice, there occurs almost no quenching. The efficiencies of aniline and pyrrole in alcoholic solution, however, are not smaller than those in aqueous solution. Moreover, pyridine has no quenching effect on the fluorescence of acridine either in aqueous or alcoholic solutions. The anomalous behavior of phenol as quencher in alcoholic solution compared with the remarkable quenching in aqueous solution, has been studied in detail for the case of DAA.

c) DAA: Mainly the effect of solvent on the fluorescence quenching by phenol, aniline and pyrrole, has been examined in detail. The pH dependence of the quenching by phenol in aqueous solution is analogous to the case of acridine, although practically no quenching occurs at pH 13. In the case of aniline and pyrrole in aqueous solution, measurement was made only at pH 5. The remarkable difference between aqueous and alcoholic solutions is as follows. Although the quenching constants in the case of aniline and pyrrole in various alcoholic solvents are in approximately the same order of magnitude as those in aqueous solution, and the quenching in alcoholic solutions shows a normal dependence on the viscosity of solvent, all values of quenching constants in the case of phenol in alcoholic solutions are ca. 0.1 (l./mole), i.e., practically no quenching occurs in this case. Here also, pyridine shows no quenching effect on the fluorescence either in aqueous or alcoholic solutions.

d) β-Naphthol: In aqueous solution some of the excited naphthol molecules dissociate into ions during the lifetime of excited molecules[9]. Therefore, in this case, the fluorescence of molecule (ultraviolet) and that of ion (blue) should be measured separately. The formula representing the relative fluorescence intensities of molecule and ion, respectively are derived easily employing the following scheme.

8) N. Mataga, Y. Kaifu and M. Koizumi, This Bulletin, **29**, 373 (1956).

9) Th. Förster, *Z. Elektrochem.*, **54**, 42, 531 (1950); A. Weller, ibid., **56**, 662 (1952); *Z. physik. Chem.*, N. F., **3**, 238 (1955).

* In these tables, when the quenching curves show some deviations from Stern-Volmer equation, the values of quenching constants are extrapolated from the regions of dilute quencher concentrations.

** Hereafter, abbreviation "S.-V. equation" will be used.

TABLE I

NITROGEN HETEROCYCLES

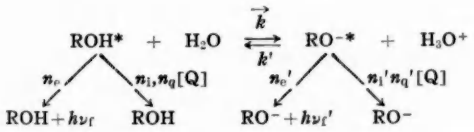
Quencher	Solvent (pH)	Quenching Constant (l./mole)*	c_h** (mole/l.)***	t(°C)****
		Quinoline		
	H_2O (1)	65	1.5×10^{-2}	~17
	H_2O (2.97)	32	3.1×10^{-2}	〃
		Acridine		
phenol	H_2O (2.97)	130 ($<2\times10^{-2}$)	7.7×10^{-5}	~20
	H_2O (6.81)	110 ($<3\times10^{-2}$)	9.7×10^{-3}	〃
	H_2O (7.73)	8 ($<4\times10^{-2}$)	1.5×10^{-2}	〃
	H_2O (11.3)	30 ($<4\times10^{-2}$)	3.6×10^{-2}	〃
	H_2O (12.9)	37 ($<5\times10^{-2}$)	3.0×10^{-2}	〃
aniline	H_2O (1.04)	10.6	9.4×10^{-2}	~14
	H_2O (7.17)	94.4	1.05×10^{-2}	〃
	H_2O (13)	32.3	3.09×10^{-2}	〃
pyrrole	H_2O (5)	77	1.3×10^{-2}	~14
		DAA		
phenol	H_2O (2.97)	21.6	4.6×10^{-2}	~21
	H_2O (4.96)	20.8	4.8×10^{-2}	〃
	H_2O (12.9)	no quenching		〃
	MeOH	0.13	(8.0)	~13
	EtOH	0.11	(9.0)	〃
	BuOH	0.12	(8.4)	〃
aniline	H_2O (5)	8	1.2×10^{-1}	~14
	MeOH	32	3.2×10^{-2}	〃
	EtOH	18	5.7×10^{-2}	〃
	BuOH	11.4	8.7×10^{-2}	〃
pyrrole	H_2O (5)	19	5.4×10^{-2}	~14
	MeOH	21	4.7×10^{-2}	〃
	EtOH	6.1	1.6×10^{-1}	〃
	BuOH	3.5	2.8×10^{-1}	〃

* An extrapolation was made in the range of the quencher concentration smaller than this value.

** The concentration of quencher at which f becomes $f_0/2$.

*** Extrapolated value in the case of very small quenching constant.

**** Temperature at which the measurement was made.



where $k'=\overleftarrow{k}[H_3O^+]$.

Then, for molecule,

$$f/f_0 = \frac{1+\alpha'[Q]}{1+\alpha[Q]+\beta[Q]^2}$$

and for ion,

$$f'/f_0' = \frac{1}{1+\alpha[Q]+\beta[Q]^2}$$

where Q represent quencher.

Therefore, $\left(\frac{f/f_0}{f'/f_0'}\right)=1+\alpha'[Q]$.

The meanings of constants α, α' and β are as follows,

$$\alpha=\frac{n\tau_q(1+k'\tau')+n_q'\tau'(1+\vec{k}\tau)}{1+\vec{k}\tau+k'\tau'}, \quad \alpha'=\frac{n_q'\tau'}{1+k'\tau'}$$

$$\beta=\frac{n_q n_q'\tau\tau'}{1+\vec{k}\tau+k'\tau'}$$

where τ and τ' are the mean lifetimes of excited molecule and ion, respectively. When $k'\sim0$, i.e., $[H_3O^+]$ is small, above equations become as follows.

$$f/f_0 = \frac{1}{1+\{n\ \tau/(1+\vec{k}\tau)\}[Q]}$$

$$\left(\frac{f/f_0}{f'/f_{0'}}\right) = 1+n_{\cdot}'\tau'[Q]$$

These equations are well satisfied by the experimental observations. Using the experimentally datermined values of $\vec{k}$, τ and τ'[9], n_q and n'_q are evaluated. The values of n_q and n'_q are almost the same, although the latter is slightly larger than the former. The dependence of n_q and n'_q on the pH values of the solution is analogous to the case of nitrogen heterocycles as fluorescers and phenol as quencher, i.e., the n_q and n'_q values become larger, the smaller the pH value is. Moreover, also in this case, the quenching efficiency in alcoholic solution is very poor compared with that in aqueous solution.

e) β-Naphthylamine: Remarkable quenching by pyridine occurs in both aqueous and methanol solution, although the quenching constant in the latter solution is somewhat less prominent. The quenching curves are well satisfied by S.-V. equation. Contrary to this, phenol does not show any quenching effect, and the efficiency of aniline as quencher is negligibly small.

f) β-Naphthylmethyl ether: In a preceding paper[3], we have reported that, no quenching effect by pyridine in benzene solution on the fluorescence of this molecule has been observed. Here it is confirmed that also in cyclohexane and acetic acid esters, the same situation prevails. In aqueous and alcoholic solutions, however, there occurs considerable quenching, respectively, almost comparable with the corresponding cases of β-naphthol molecule.

g) *N,N*-Dimethyl-α-naphthylamine: The circumstance is analogous to the case of β-naphthylmethyl ether. In benzene solution, the fluorescence of this molecule is not influenced by pyridine[3]. In aqueous solution, however, the fluorescence is quenched by pyridine considerably.

TABLE II

β-NAPHTHOL-PYRIDINE

Solvent (pH)	n_q	n'_q	t(°C)
H_2O (3.95)	3.6×10^9	4.2×10^9	~16
H_2O (7.17)	1.7×10^9	3.1×10^9	〃

TABLE III

β-NAPHTHYLAMINE-PYRIDINE

Quencher	Solvent	Quenching Constant	t(°C)
pyridine	H_2O*	63	~16
	MeOH	26	〃

*pH is not controlled by buffer.

Discussion and Concluding Remarks

In previous papers[2,6,7], we have reported the fact that, in the case of nitrogen heterocycles, the difference in the emitting π-electronic state leads to the different behavior of these nitrogen heterocycles in fluorescence quenching by the near-by existence of halogen atoms. Some qualitative considerations by means of analogy to the π-electronic structures of parent hydrocarbons were given[2], and a quantitative argument has been given on the basis of a theoretical computation[6,7]. In the present case, however, no such effect of emitting π-electonic state on the fluorescence quenching is observed, and phenol quenches the fluorescence of quinoline as well as acridine and DAA almost equally well. Therefore, with the present type of fluorescence quenching which is caused by the interaction between π-electron systems in the excited state, ^3L_b state may not concern so severely, although the detailed microscopic mechanism of the quenching is not so clear. Now, in the following, some arguments will be given from two standpoints, i.e., the most effective combination of fluorescer and quencher, on the one hand, and the effects of solvents on the quenching efficiency, on the other hand.

A. Fluorescence Quenching and Acid-Base Relation. Phenol, aniline and pyrrole quench severely the fluorescence of nitrogen heterocycles such as quinoline, acridine and DAA. Contrary to this, pyridine does not show any quenching effect on the fluorescence of the nitrogen heterocycles.

Moreover, the fluorescence of naphthol as well as naphthylamine is quenched by pyridine effectively. Phenol and aniline, however, scarcely quench the fluorescence of these naphthalene derivatives at all. Thus, it is evident that the most efficient fluorescer-quencher pair is in acid-base or proton donor-acceptor relation, and roughly speaking, there exists a parallelism between the fluorescence quenching due to hydrogen bonding in non-polar solvent and the present case.

From this fact, we might be allowed to suppose that some analogous mechanism to the case of fluorescence quenching due to hydrogen bonding in non-polar solvent[1],

may prevail also in the quenching of present type, although the circumstance is more complicated.

B. Effects of Solvents on the Efficiency of Fluorescence Quenching. Pyridine does not quench the fluorescence of β-naphthylmethyl ether as well as *N,N*-dimethyl-α-naphthylamine, in benzene, cyclohexane and acetic acid esters. In aqueous and alcoholic solutions where the hydrogen bond between solvent molecules and also between solvent and solute molecules exist, however, the fluorescence of these molecules is quenched remarkably to almost the same extent as in the case of naphthol and naphthylamine, respectively. The important role of hydrogen bonding in the fluorescence quenching of this case is implicit in the fact that, only in the associating liquids such as water and alcohol, the fluorescence is quenched efficiently.

Another remarkable example of the solvent effects is that the behavior of the phenol-nitrogen heterocycles or pyridine-naphthol system in alcoholic solution is very different from that in aqueous solution.

In contradistinction to the severe quenching in aqueous solution, the quenching in alcoholic solution is very slight. Although the cause of this remarkable difference is not clear, we can not but ascribe it to the difference in the liquid structure, viz., the very extensive hydrogen bonding in water on the one hand and the less extensive hydrogen bonding in alcohol on the other hand might have some connection with this phenomenon.

Summary

The acid-base relation in the fluorescence quenching in aqueous and alcoholic solutions, due to the interaction between π-electron systems in the excited state, has been pointed out. Roughly speaking, this is parallel with the fluorescence quenching due to hydrogen bonding between the π-electronic fluorescer and quencher in non-polar solvent. Remarkable solvent effects on the quenching efficiency have been found and some important roles of hydrogen bonding in this phenomenon have been suggested.

The author expresses his sincere gratitude to Professor S. Mizushima of Tokyo University for his encouragement. He is also grateful to Professor M. Koizumi of Tohoku University for his interest in the present work. He expresses his thanks to Professor R. Fujishiro for his encouragement during this investigation. He also expresses his appreciation to Dr. S. Nagakura of Tokyo University and Dr. H. Tsubomura of Tokyo University for their discussions. His thanks are especially due to Miss S. Tsuno for her experimental assistance throughout this investigation. His thanks are also due to Miss S. Wada for typewriting this paper.

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On the Constitution of Myoporone (Natural Furan Derivatives. II.**)*

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(Received December 14, 1957)

The essential oil of the genus *Myoporum*, endemic to Australia and New Zealand, was examined by several investigators. McDowall[1] first isolated ngaione from the volatile oil of *Myoporum laetum* Forst. in 1925. Subsequently Birch, Massy-Westropp and Wright[2] isolated the same substance and 3-furoic acid from a specimen of *M. acuminatum*. They also examined the volatile oil of two other specimens of *M. acuminatum* and found that these oil contained at most traces of

* T. Kubota and T. Matsuura, *Chemistry and Industry*, **1957**, 491.

** Part I. T. Matsuura, This Bulletin, **30**, 430 (1957).

1) F. H. McDowall, *J. Chem. Soc.*, **1925**, 2200.

2) A. J. Birch, R. A. Massy-Westropp and S. E. Wright, *Australian J. Chem. Soc.*, **6**, 385 (1953).

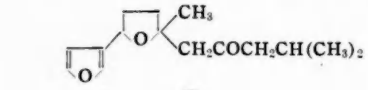
ngaione and an α,β-unsaturated furanoketone, $C_{15}H_{20}O_2$.

Ngaione was extensively investigated by several workers[3], but no complete formula has yet been put forward. Recently, we have succeeded in demonstrating that ngaione has the structure I[4], namely the enantiomorph of (+)-ipomeamarone, the toxic bitter principle of black rotten sweet potato. In connection with these works we have recently examined the essential oil from the Japanese *M. Bontioides* A. Gray (the only *Myoporum* found in Japan), and have found that ngaion is contained only in a small amount and the major constitutent is a new terpene ketone (the yield from undried leaves, ca. 0.2%). This ketone has been designated myoporone and the elucidation of its structure will be reported herewith. The essential oil contained also an unsaturated hydrocarbon, C_nH_{2n} of m. p. 63~64°C.

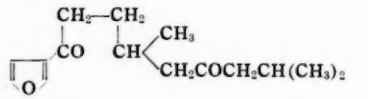
Myoporone (b. p. 117~119°C/10^{-2} mm.; n_D^{21} 1.4770) is a pale yellow oil with a slightly bitter taste, and shows no optical rotation, at D line, but its 2,4-dinitrophenylhydrazone (α-form, see below) has $[\alpha]_D^{28}$ −28.2°***.

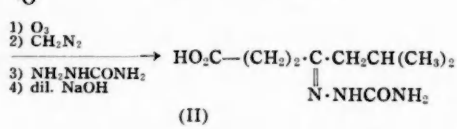
It gives a purple coloration with Ehrlich's reagent, a pale brown coloration with concentrated hydrochloric acid, decolorized potassium permanganate, and yield a dark red Liebermann reaction. The molecular formula is $C_{15}H_{22}O_3$, and two bis-2,4-dinitrophenylhydrazones, $C_{27}H_{30}O_9N_8$ are obtained. The α-form has red color and melts at 193°C, while β-form is orange-yellow and turns into red at 143~145°C and melts at 193°C. These substances seem to be dimorphous[5]. Infrared absorptions of myoporone in Nujol are shown at 3.19 (furan), 5.88 (ketone), 5.95 (conjugated ketone), 6.41 (furan), 6.63 (furan) and 11.45 μ (furan).

Oxidative degradation of myoporone ozonide followed by esterification of the acidic fraction yielded a methyl ester, b. p. 88~90°/10^{-2} mm., n_D^{18} 1.4378, λ_{max}^{nujol} 5.77 and 5.84 μ. Conversion of this ester into semicarbazone and subsequent hydrolysis gave a semicarbazone of ketonic acid, m. p. 139~140°C ($[\alpha]_D^{18}$ −9.18), which was found to be identical with the previously synthesized semicarbazone of dihydroanhydroipomic acid (III)[6] by the infrared absorption spectra in Nujol. These facts lead to structure II for myoporone and this has been confirmed by sythesis.



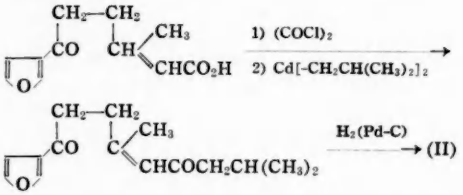
(I)





(II)

The synthesis of (±)-myoporone was started from the previously synthesized 2-methyl-4-(3'-furoyl)-1-butene-1-carboxylic acid (IV)[7] and effected according to the following sequence.



The melting point of the 2,4-dinitrophenylhydrazone (red, α-form) of the synthetic (±)-myoporone was 208~210°C, but its infrared absorption spectrum in Nujol was completely in agreement with that of α-form of 2,4-dinitrophenylhydrazone of the natural product.

Myoporone may probably be produced in vivo through intramolecular oxido-reductive cleavage of the tetrahydrofuran ring of ngaione (I). The isolation of ngaione ((−)-ipomeamarone), myoporone and 3-furoic acid[2] from the essential oil of *Myoporum*, and the isolation of (+)-ipomeamarone (I), batatic acid[8] (VI) ipomeanine[9] (VII) and 3-furoic acid

3) F. H. McDowall, *J. Chem. Soc.*, **1927**, 731; **1928**, 1324; C. W. Brandt and D. J. Ross, ibid., **1949**, 2778; A. J. Birch, R. A. Massy-Westropp, S. E. Wright, T. Kubota and T. Matsuura, *Chemistry & Industry*, **1954**, 175.

4) T. Kubota and T. Matsuura, ibid., **1956**, 521.

*** In the preliminary paper (T. Kubota and T. Matsuura, ibid., **1957**, 491), we reported that natural myoporone is in racemic form, because of its lack of optical activity at D line. This measurement was performed by the courtesy of Professor Y. Hirata, Nagoya University.

5) W. Dirscherl and H. Nahm, *Ber.*, **73**, 448 (1940).

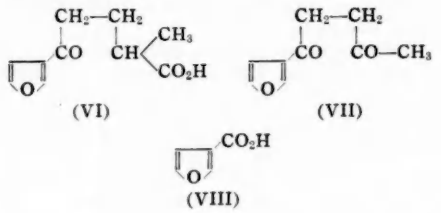
6) T. Kubota and T. Matsuura, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **74**, 105 (1953).

7) T. Kubota and T. Matsuura, *Chemistry & Industry*, **1956**, 521; T. Matsuura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 248 (1956).

8) T. Kubota and K. Naya, ibid., **77**, 86, 252 (1956).

9) T. Kubota and N. Ichikawa, ibid., **75**, 450 (1954).

(VIII)[10] from black rotten sweet potatoes is quite interesting in relation to the metabolism of terpenes and β-substituted furan derivatives in plant.



(VI) (VII) (VIII)

Experimental

Isolation of Myoporone.—Leaves (10.06 kg.) of *Myoporum bontioides* A. Gray, which were collected at fructifying time in Tanegasima Island, Kagoshima Prefecture, Japan, were roughly cut and digested in methanol (15 l.) for about three months. After distilling off the solvent, water was added, and the liquor was extracted with ether (500 cc.×4). The ethereal solution was concentrated to a small volume and was shaken with sodium bicarbonate solution. From the bicarbonate solution, a small amount of the acidic matter was obtained. Evaporation of the ethereal solution left a brownish green liquid (45.5 g.). Vacuum-distillation of the liquid gave a yellow liquid (A; 27.1 g.), b. p. 90~150°C/10^{-2} mm. and n_D^{23} 1.4750, which was fractionally distilled as shown in Table I.

Table I

	Fraction	b. p./10^{-2} mm.	Yield	n_D^{23}	Color
A	-I	<121°	1.8 g.	1.4512	yellow
	-II	121 ~125°	23.4 g.	1.4752	yellow
	-III	125°<	1.1 g.	1.4718	yellow
	Fraction	b. p./10^{-2} mm.	Yield	$n_D^{23.5}$	Color
II	-I′	<113°	1.7 g.	1.4780	yellow
	-II′	113 ~116°	20.5 g.	1.4733	yellow
	-III′	116°<	0.8 g.	1.4685	yellow
	Fraction	b. p./10^{-2} mm.	Yield	n_D^{21}	Color
II′	-I″	<117°	1.4 g.	1.4776	pale yellow
	-II″	117 ~119°	13.8 g.	1.4770	pale yellow
	-III″	119°<	3.2 g.	1.4760	pale yellow

The fraction (II″) consists of almost pure myoporone.

Extraction of leaves, which were collected at flowering time, gave the same results as described above.

Isolation of C_nH_{2n}-hydrocarbon. — Dried leaves (430 g.) of *Myoporum bontioides* A. Gray were digested with ether (4 l.). Evaporation of the ethereal solution gave a brownish green semi-solid (14 g.). When the semi-solid was well mixed with ethanol (60 cc.) and filtered, there were obtained crystals (3.7 g.) which crystallized from ethanol in wax-like colorless plates, m. p. 63~65°C.

Anal. Found: C, 85.85; H, 14.71%. Calcd. for C_nH_{2n}: C, 85.63; H, 14.37%.

Distillation of the liquid part of the extract gave a liquid (1.0 g.), b. p. 105~120°C/10^{-2} mm. and n_D^{17} 1.4890. It showed a positive reaction with the Ehrlich's reagent and its infrared spectrum showed the presence of furan ring (3.18, 6.41, 6.65 and 11.42 μ), hydroxyl group (2.85 μ), and two carbonyl groups (5.88 and 5.98 μ) in the molecule, but its semicarbazone could not be obtained in crystalline state.

Detection of Ngaione. — The fraction II′ (0.5 g.), semicarbazide hydrochloride (0.5 g.), and potassium acetate (0.5 g.) were dissolved in dilute ethanol and the whole was kept overnight. Water was added and the resulting sticky mass (0.7 g.) was collected and dried. It was dissolved in benzene (20 cc.) and was purified by chromatography with alumina. From the benzene eluate, a small amount of crystal was obtained. It was recrystallized from benzene and light petroleum as colorless plates, m. p. 130~132°C, which showed no depression on admixture with the semicarbazone of ngaione, kindly supplied by Professor A. J. Birch, m. p. 132~133°C. The further elution with benzene-ethanol gave a semicarbazone as a syrup, which did not crystallize.

Bis-2,4-dinitrophenylhydrazones of Myoporone. — When the fraction II″ (0.4 g.) was mixed with a solution of 2,4-dinitrophenylhydrazine (1.0 g.) in concentrated sulfuric acid (1 cc.) and ethanol (100 cc.), orange red precipitates made their appearance in a few minutes. After standing for 2 hr., the precipitates were filtered. Yield 0.5 g. Repeated treating of the precipitates with ethyl acetate gave red crystals, which was slightly soluble in ethyl acetate. They were recrystallized from benzene to afford red prisms, m. p. 193°C, which were designated as α-bis-2,4-dinitrophenylhydrazone $[\alpha]_D^{23}$ −28.2 (Chloroform, C=0.18).

Anal. Found: C, 53.20; H, 4.92; N, 18.89%. Calcd. for $C_{27}H_{30}O_9N_8$: C, 53.2; H, 4.92; N, 18.33%.

From the mother liquor of the above recrystallization, a mixture of the red α-bis-2,4-dinitrophenylhydrazone and yellow needles separated, and the latter were collected mechanically, which was designated as β-bis-2,4-dinitrophenylhydrazone. It melted at 193°C after changing to red color at 143~145°C. Recrystallization of β-compound from benzene gave α-compound and its mother liquor deposited a mixture of α- and β-compounds.

Anal. Found: N, 18.64%. Calcd. for $C_{27}H_{30}O_9N_8$: N, 18.33%.

Ozonization of Myoporone. — Myoporone (2.0 g.) in chloroform (30 cc.) was saturated with ozone and the solvent was evaporated under reduced pressure. The resulting ozonide was decomposed under ice-cooling with a bichromate

10) T. Kubota, H. Yamaguchi, K. Naya and T. Matsuura, ibid., **73**, 897 (1952).

mixture, the latter being composed of the admixture of potassium bichromate (3.2 g.), concentrated sulfuric acid (2 cc.), and water (20 cc.). After two days' standing the mixture was extracted with ether. The ethereal solution was extracted with a bicarbonate solution. The acidic substance, obtained from the bicarbonate extract, was methylated with diazomethane in ether. Distillation of the methyl ester gave a colorless liquid, b. p. 88~90°C/10^{-2} mm. and n_D^{18}1.4378. Its refractive index coincides with that of synthetic methyl dihydroanhydroipomate, $n_D^{17.5}$ 1.4390[6]. IR-spectrum: 5.77 μ (ester) and 5.84 μ (ketone).

This methyl ester (0.25 g.), semicarbazide hydrochloride (0.2 g.), and potassium acetate (0.2 g.) were dissolved in dilute ethanol and, after standing overnight, water was added. The precipitates, which had separated in the meanwhile, were collected through decantation and then hydrolyzed with 1 N sodium hydroxide (2 cc.). Acidification of the hydrolysate gave white precipitates, which were recrystallized from ethanol. Colorless plates, m. p. 139~141°C. This substance was identical with the synthetic dihydroanhydroipomic acid semicarbazone, i. e. 3,7-dimethyl-5-keto-octane-1-carboxylic acid semicarbazone, m. p. 140~141°C in infrared spectrum. No remarkable depression of melting point was recognized on admixture of both samples.

Synthesis of Myoporone

1-Isovaleryl-2-methyl-4-(3'-furoyl)-1-butene (V). — 2-Mtheyl-4-(3'-furoyl)-1-butene-1-carboxylic acid (IV), m. p. 103~104°C[11], was converted into the acid chloride with oxalyl chloride, according to the method of Barkley et al.[12] The acid (4.2 g.) was dissolved in absolute methanol (20 cc.) and neutralized with 1 N sodium methoxide solution in methanol. After the solvent was evaporated in vacuo, dry benzene was added and evaporated again to dryness in vacuo. The resulting sodium salt was suspended in dry benzene (25 cc.) and oxalyl chloride (4 g.) in benzene (10 cc.) was added in portions under ice-cooling. After the mixture was kept at 40°C for 20 min., benzene and excess of oxalyl chloride were distilled off under reduced pressure. The acid chloride, which was obtained as brown liquid, was dissolved in benzene (20 cc.).

To a Grignard solution, which was prepared from isobutyl bromide (5.5 g.), magnesium (1.0 g.), and absolute ether (30 cc.), dried cadmium chloride (4.0 g.) was added under ice-cooling, and the mixture was refluxed until a Gilman-Schulz test was negative. After distillation of ether, benzene (30 cc.) was added.

To the stirred diisobutyl cadmium solution thus obtained, the acid chloride solution in benzene was rapidly added with constant refluxing. The mixture was refluxed for 30 min. or more and then was decomposed with dilute hydrochloric acid under ice-cooling. The organic layer was separated, washed with a bicarbonate solution, dried and evaporated. Twice distillations of the resulting dark brownish liquid (3.0 g.) gave a pale yellow liquid (1.2 g.), b. p. 119~122°C/10^{-2}mm. and n_D^{12} 1.4925, and its color changed to brownish yellow on standing. IR-spectrum: 3.18 (furan), 5.96 (furyl ketone and α,β-conjugated ketone), 6.08 (double bond), 6.41 (furan), 6.63 (furan), and 11.44 μ (furan).

1-Isovaleryl-2-methyl-4-(3'-furoyl)-butane. (Myoporone).—The above obtained liquid (0.28 g.) was dissolved in ethanol (10 cc.) and hydrogenated in the presence of 5% palladium-charcoal (0.1 g.). After 1.1 moles of hydrogen were absorbed (about one hr.), the catalyst was filtered off. To the filtrate 2,4-dinitrophenylhydrazine (0.4 g.) in ethanol was added in the presence of sulfuric acid. Twice recrystallizations of the resulting precipitates from ethyl acetate gave a red prism, m. p. 208~210°C, which showed no depression on admixture with α-bis-2,4-dinitrophenylhydrazone of myoporone, m. p. 193°C and was identical with α-compound in infrared spectrum.

The writers wish to express their thanks to Professor S. Miki, Department of Biology, Osaka City University, for collection and identification of *Myoporum Bontioides* A. Gray. Cordial thanks are also due to Mr. T. Kurokawa, Kagoshima Prefectural Industrial Research Institute and Mr. T. Uehara, Tanegashima Branch of the Kyushu Goverment Agriculture Experiment Station, for gathering the same plants.

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11) T. Matsuura, ibid., **78**, 389 (1957).
12) L. Barkley et al., *J. Am. Chem. Soc.*, **76**, 5017 (1954).

SHORT COMMUNICATIONS

*Fractionation of Sulfur Isotopes during Oxidation**

By Iwaji IWASAKI, Hiroshi FUKUTOMI and Hikaru SHIMOJIMA

(Received February 10, 1958)

Many studies[1] on the abundance of sulfur isotopes in natural sulfur compounds have been already carried out and it was learned that the heavy isotope, sulfur-34 is generally enriched in the compounds of higher oxidation state. When the difference of oxidation state between two compounds is greater, the fractionation of isotopes is more prominent.

An experiment was carried out to make clear the process of the fractionation of sulfur isotopes during oxidation and to explain the distribution of sulfur isotopes in nature using radioisotope, sulfur-35 as tracer. In these experiments radioactive zinc sulfide was prepared by introduction of hydrogen sulfide labelled with ^{35}S into zinc acetate solution. The precipitate of zinc sulfide was filtered and washed with ammonium acetate solution and suspended in ammoniacal solution. A part of the suspended sulfide, about one tenth of the total, was first oxidized to sulfate by adding carefully a definite volume of bromine water into the solution. The residual sulfide was filtered off, and the sulfate in the filtrate was precipitated as barium sulfate. The care against the fractional precipitation of sulfur isotopes, that had been described by the authors[2], was also taken in this case. The residual sulfide precipitate was again suspended in ammoniacal ammonium acetate solution and partly oxidized with bromine water by the same manner as described above. The experiment was carried out sucessively till all the sulfide was consumed. About ten samples of barium sulfate for the determination of the radioactivity were obtained.

Their radioactivities were measured by the infinite-thickness method. Some of the experimental results obtained are shown in Fig. 1. If the fractionation of sulfur isotopes had not taken place during these processes, these samples should have had

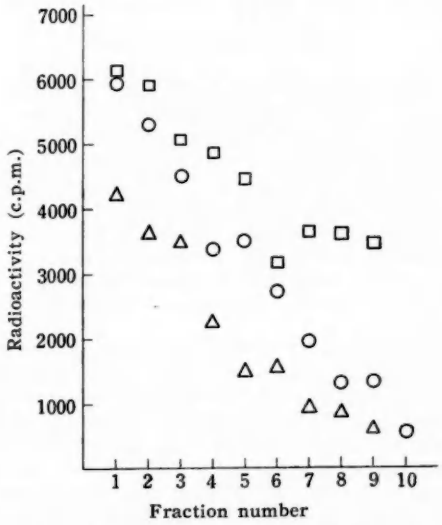

Fig. 1. Variation in radioactivity of barium sulfate obtained in succession from one suspension of zinc sulfide by fractional oxidation.
○ at 4°C △ at 25°C □ at 65°C

the same specific activity. However, there is a considerable and regular variation in their radioactivity and the earlier barium sulfate obtained in one series of fractional oxidation from one suspension has remarkably larger specific activity than that of the later. These variations are evidently beyond the possible experimental error. It might be too early to give definite conclusions on the mechanism of fractionation of sulfur isotopes from these results, but the isotope effect will be considered as the most important factor for the explanation of these phenomena and the fractionation of sulfur isotopes

* This report was presented at the 1st Symposium of Radiochemistry sponsored by The Chemical Society of Japan, December, 1957.

1) H. G. Thode et al., *Can. J. Research*, **B27**, 361 (1949); **B28**, 567 (1950); A. P. Vinogradov et al., *Geokhimia*, **1**, 96 (1956); H. Sakai, *Geochim. et Cosmochim. Acta*, **12**, 150 (1957).

2) I. Iwasaki, S. Ikeda, H. Shimojima, H. Fukutomi and H. Sugano, *Annual Report of the Radioisotopes in Japan*, **3**, 1 (1956).

during oxidation seems to be one of the most important factors on the enrichment of the heavy sulfur isotope into the compounds of high oxidation state.

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*Fractionation of Sulfur Isotopes during Reduction**

By Iwaji Iwasaki, Hikaru Shimojima and Hiroshi Fukutomi

(Received February 10, 1958)

The experimental and the theoretical studies are being made by the present authors on the natural abundance and their variation of stable isotopes of sulfur. In the previous report[1] a great fractionation of the heavy isotope (^{35}S) during oxidation of sulfide was reported. The present experiment has been carried out to make clear the fractionation of sulfur isotopes during reduction using sulfur-35 as tracer.

Barium sulfate labelled with sulfur-35 was reduced in a carbon dioxide stream with tin(II)—strong phosphoric acid reagent[2]. Hydrogen sulfide evolved from the reaction mixture was taken out of the reaction system with carbon dioxide. This gas was led to two absorbing cells in series. In the first cell, was placed an accurate, known amount of aqueous zinc acetate solution just enough to make precipitate of zinc sulfide for the radioactivity measurement. In the second cell, alkaline suspension of basic cadmium carbonate was put in to absorb and detect the rest of hydrogen sulfide which comes out from the first cell. The detection of hydrogen sulfide coming in the second cell was easily made by observing the formation of yellow cadmium sulfide. When sufficient zinc sulfide was obtained, the gas-flow of hydrogen sulfide and carbon dioxide from reaction system was switched to another set of two absorbing cells using a three-way stopcock.

In this way, many fractions of small and equal amount of zinc sulfide were obtained. The specific counting rate of each sample was measured by the infinite-thickness method. In order to be sure to detect a small variation in the specific counting rate, hydrogen sulfide evolved in the very beginning of the reaction was carefully sampled, and sixty fractions were obtained during a run of reduction experiment. Some of the results obtained are shown in Fig. 1. There found a regular and remarkable variation in their specific counting rate and the earlier

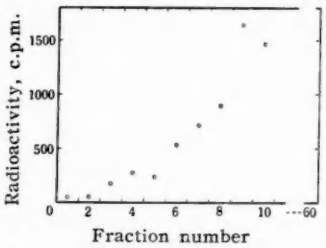

Fig. 1. Variation in radioactivity of each fraction of zinc sulfide obtained in succession from one barium sulfate sample by fractional reduction.

sulfide obtained in a series of a fractional reduction from barium sulfate has remarkably smaller specific counting rate than that in the later stage over the possible experimental error.

The fractionation of sulfur isotopes during oxidation was previously reported[1]. In this case, the radioactive sulfur isotope (^{35}S) was enriched in the products of earlier stage of oxidation. Thus the result agrees with the conclusion shown in the present report.

As the fractionation of radioactivity is quite remarkable in both reduction and oxidation, it would be possible to apply successfully in a larger scale to the purpose of enriching stable isotopes as well as radioactive ones. An experiment is planned to determine the extent of the differentiation between the stable isotopes of sulfur-32, 34 and 36 in the same sort of treatment of sulfur compounds.

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* Presented by H. Shimojima before the 8th Annual Meeting of the Chemical Society of Japan on April 3, 1955.

1) I. Iwasaki, H. Fukutomi and H. Shimojima, This Bulletin. **31**, 495 (1958).
2) T. Kiba and I. Kishi, ibid. **30**, 44 (1957).

The Solubilization of Benzene in Aqueous Soap-Alcohol Solution

By Kōzō Shinoda and Hideo Akamatu*

(Received January 6, 1958)

One of the most outstanding properties of detergent solution is its ability to solubilize polar or non-polar oil above the critical micelle concentration[1,2]. Klevens[3,4] investigated the effect of added alcohols, salts and the other additives on the solubilization of *n*-heptane in potassium tetradecanoate solution and found a very marked increase in the solubilization of *n*-heptane.

The present paper reports the effect of added alcohols and salts on the solubilization of benzene in potassium dodecanoate solution at 25°C.

Experimental.—The solubilization end point was determined by transmission measurements with the same procedure described by Stearns et al.[1] Butanol, *iso*-pentanol, hexanol, cyclohexanol and octanol were purified materials[5]. Dodecanoic acid was purified by vacuum distillation. The solubilization of benzene in aqueous potassium dodecanoate was the same with that reported by Stearns et al.[4]

Results and Discussion.—*The Effect of Added Alcohols on the Solubilization.* The effect of added alcohols on the solubilization of benzene in aqueous potassium dodecanoate was plotted in Fig. 1.

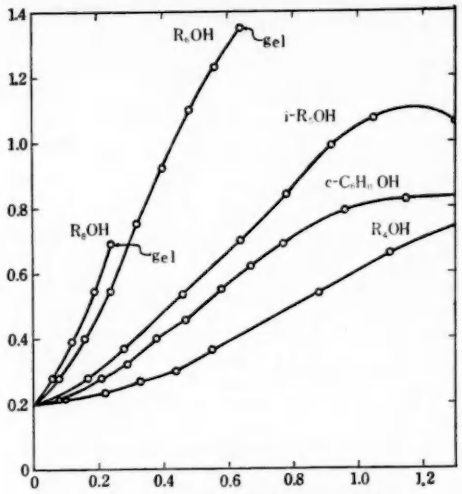

Fig. 1. The effect of added alcohols on the solubilization of benzene in potassium dodecanoate, 0.285 mole/l., solution ordinate: moles of benzene per 1000 cc. of solution.
R_4OH, butanol; i-R_5OH, *iso*-pentanol; R_6OH; hexanol; R_8OH, Octanol; C-$C_6H_{11}OH$, Cyclohexanol.

It is evident that 1) the amount of benzene solubilized markedly increased by the addition of alcohols, 2) the longer chain alcohol is much more effective than shorter chain alcohol in promoting solubilization and 3) the effect of added alcohol is greater than that of corresponding fatty acid soaps. This suggests that the penetrated long-chain alcohol increases the micellar size and that by decreasing the electrical repulsive force of micelle-forming ion the aggregation number of micelle forming ion also increases, causing a marked increase in micellar size and solubilizing power. In the case of cyclo-hexanol and *iso*-pentanol the amount of benzene solubilized showed maximum and then gradual decrease. In the case of hexanol and octanol, gel formation occurred at a relatively low alcohol concentration, therefore the solubilization was determined only at the lower concentration.

Estimation of the Micellar Charge from the Solubilization Measurements. The effect of soap concentration on the solubilization of benzene per mole of micellar potassium dodecanoate was determined and plotted in Fig. 2[6]. The effect of potassium chloride on the solubilization of benzene in aqueous potassium dodecanoate, 0.192 mole/l., was also determined and plotted in Fig. 2.

It is supposed that the increase of solubilization of benzene per mole of soap is essentially the same phenomenon in both systems. Namely, the increase in the counter-ion concentration, due to the increase in soap concentration or added salts, decreases the electrical potential on the micelle surface and tends to increase

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1) R. S. Stearns, H. Oppenheimer, E. Simon and W. D. Harkins, *J. Chem. Phys.*, **15**, 496 (1947).
2) M. E.L. McBain and E. Hutchinson, "Solubilization", Academic Press Inc., New York, 1955.
3) H. B. Klevens, *J. Chem. Phys.*, **17**, 1004 (1949).
4) H. B. Klevens, *J. Am. Chem. Soc.*, **72**, 3581, 3780 (1950).
5) K. Shinoda, *J. Phys. Chem.*, **58**, 1136 (1954),
6) The concentration of micellar soap was calculated, subtracting the single ion concentration from the stoichiometric concentration. The solubility of benzene in water was subtracted from the total amount of benzene solubilized to calculate the actual amount of benzene solubilized in the micelle.

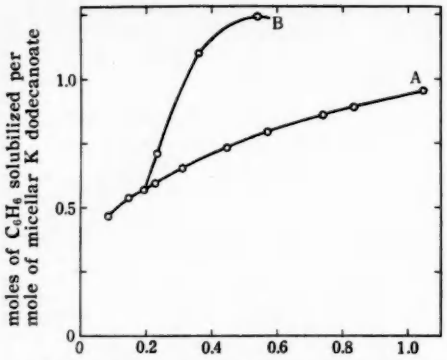

Fig. 2. A. the effect of soap concentration and B. the effect of counterion concentration on the solubilization of benzene in potassium dodecanoate solution at 25°C.

the aggregation number. If the micelles become larger, the amount of non-polar oil solubilized per micelle forming ion may increase. In a soap solution, the free counter-ion does not increase as expected from its stoichiometric concentration, since the counter-ion mostly adheres on the micelle surface. If we assume that the inter-micellar force is negligible, the amount of benzene solubilized per mole of micellar soap depends only on the concentration of counter-ion. From the comparison between curves A and B, we see that the amount of benzene solubilized per mole of micellar soap increases as slowly as about one-fifth times in curve A, therefore it can be concluded that about 80% of the counter-ion is fixed on the micelle surface, i.e., the degree of "ionization" of micelle is about 0.2 at about 0.2~0.3 mole/l. Recalculating Klevens's[4] and Stearn's[1] results with the same procedure, the degree of ionization of micelle was evaluated as 0.25 in the case of potassium tetradecanoate at about 0.5 mole/l.

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E. M. F. Change in the Thermo Cell due to Soret Effect

By Kazuo Sasaki and Shigeo Nagaura

(Received November 25, 1957)

Thermo cell is defined as a cell in which two identical electrodes are kept at different temperatures so as to form a steady temperature gradient in the electrolyte solution. In such a cell, it has long been realized that the electro-motive force (emf) should change as thermal diffusion proceeds and, at a stationary state, should reach a steady value E_∞ corresponding to Soret equilibrium. Although many experimental investigations have been reported about thermo-cell emf, almost all the data refer to the initial emf (E_0), which is the emf of a cell of uniform concentration; that is the state at which no change in concentration due to thermal diffusion has yet been appreciable.

Non-stationary change of thermo-cell emf was first confirmed by Agar and Breck[1] by an ingenious method using amalgam electrode; however, the measurements were restricted only to some special ions which were rather unfamiliar in this field of investigation.

We have long been interested in this problem and engaged in solving it; lately we observed a similar example of the phenomenon using silver-silverchrolide electrode with which most of the previous investigators have been concerned.

The emf change due to Soret effect can not be detected by an ordinary cell construction, which is used to measure the initial emf; because the large volume of the bulk solution in the electrode chamber makes the small change in composition indistinctive. Thus following precautions were taken into account for cell design;

1) the electrodes must be placed directly in the diffusion path,

2) the length of the diffusion path, i.e. the inter-electrode distance should be so determined that the time required for the establishment of the diffusion equilibrium (steady state) will accord with the restriction of the actual measurement,

3) temperature gradient must be linear throughout the diffusion path.

Along these requirements we designed

1) J. Agar and W. Breck, *Trans. Faraday Soc.*, 53, 167 (1957).

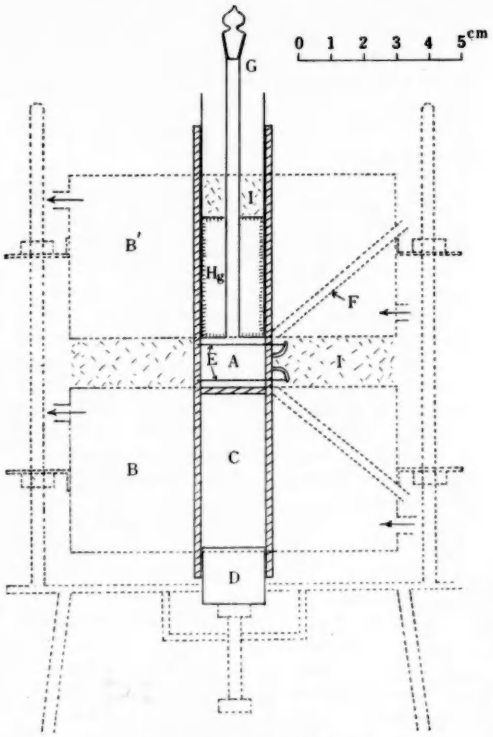

Fig. 1. Cell assembly

E Electrode; A Diffusion path; B, B' Water jacket;
C Heat conducting space (water is enclosed);
Hg Heat conducting space (containing mercury);
D Rubber stopper; F Thermocouple pocket;
G Filling tube; I Insulator.

several types of cells and tested their usefulness. A very simple cell, which is schematically shown in Fig. 1, has eventually revealed itself to be quite useful. Its detailed information will be reported in the succeeding paper.

The temperature gradient was set up by means of two jackets fitted tightly to the body of a cylindrical cell; water of a given temperature could be circulated through them.

As the first step of the present investigation, we took hydrochloric acid in different concentrations as a test solution. The fundamental feature of emf change with time is graphically shown in Fig. 2. In the figure the temperature change in the cell is also drawn, which was obtained by means of differential thermocouple. As

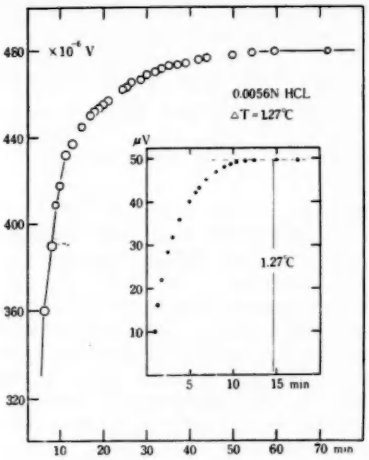

Fig. 2. Emf change with time (min.).
Empty circle: Emf of the cell,
Full circle: Thermocouple reading

is clearly seen from the figure, the emf changes rapidly at the first stage, in which a steady temperature gradient is established. After the temperature gradient has come stationary, the emf increases continuously, although not so rapid as before, exhibiting exponential diffusion behavior and reaches a steady value at a finite period of time. This behavior accords well with the theoretical expectation derived by Bierlein[2]: when the emf is plotted against $\sqrt{t}$ for the initial stage of thermal diffusion (not to be confused with the stage at which the heat conduction is not yet stationary), a straight line is obtained with a good approximation, whilst for the final stage log $(E_\infty - E_t)$ has a linear dependency upon t. These relationships are drawn in Figs. 3 and 4. In contrast to Agar and Breck's result, the reverse curve, which can be obtained

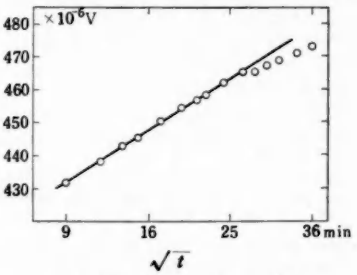

Fig. 3. Emf against $\sqrt{t}$

2) J. Bierlein, *J. Chem. Phys.*, **23**, 10 (1955).

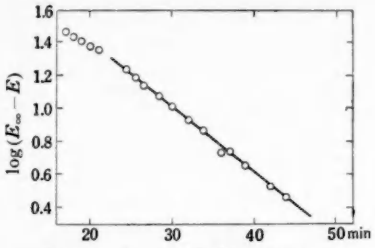

Fig. 4. Log (E_∞—E) against t.

when the temperature gradient is cut off, does not show the symmetric form against the curve of non-isothermal change but is somewhat erroneous. This problem, however, is left for further study.

A similar relation was observed for hydrochloric acid solution of various concentrations. Detailed information and theoretical explanation will successively appear.

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The Ultraviolet Absorption Spectra of the Molten and Solidified Mixed Salt Systems $NaNO_2$–$NaNO_3$, $NaCl$–$CdCl_2$

By Kaoru Sakai

(Received February 22, 1958)

According to the previous researches[1-3], it was found that the position of absorption edges of aqueous solutions which contain two component salts is shifted toward longer wave length than that of solutions each containing one of the components alone, provided that the two component salts react with each other and produce some kind of complex. Therefore we tried to find out the same phenomena[4,5] in the case of complex formation of the molten salt systems.

The experimental method is the same as that published by the present author previously[6], and the data are shown in Fig. 1 ($NaNO_2$–$NaNO_3$), and Fig. 2 ($NaCl$–$CdCl_2$), where are given the isotherms showing the relationship between the position of absorption edge and the component.

The phase diagram[7] of the $NaNO_2$–$NaNO_3$ system indicates solid solution over almost the entire range of composition, and the isotherms of its electrical

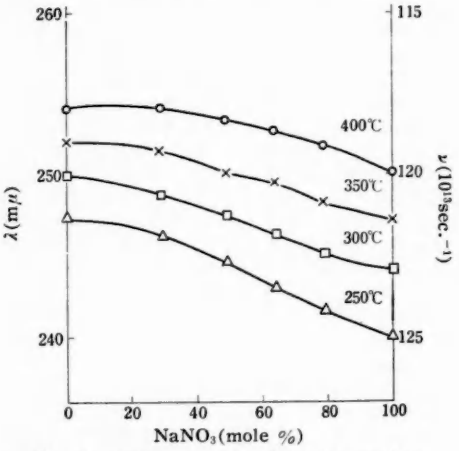

Fig. 1. Isotherms of absorption edges of the $NaNO_2$—$NaNO_3$ system.

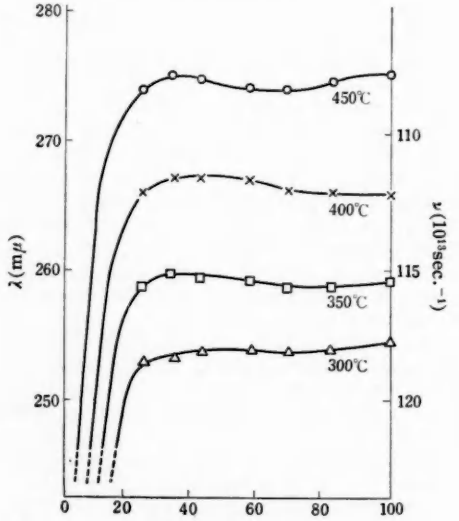

Fig. 2*. Isotherms [of absorption] edges of the NaCl—$CdCl_2$ system.

1) Y. Shibata, B. Inoue and Y. Nakatsuka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Kaishi*), **42**, 983 (1921); Y. Shibata, and B. Inoue, ibid., **43**, 722 (1922).
2) P. Job, *Compt. rend.*, **180**, 928 (1925); **182**, 1622 (1926); *Ann. chim.*, **9**, 143 (1927).
3) R. Tsuchida, This Bulletin, **10**, 27 (1936).
4) K. Sakai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1108 (1957).
5) K. Sakai, ibid., **78**, 1257 (1957).
6) K. Sakai, ibid., **77**, 1731 (1956).

conductance[7] do not exhibit any appreciable change, i. e., there is no evidence of complex formation. On the other hand, the phase diagram[8] of the $NaCl$–$CdCl_2$ system shows the formation of one incongruently melting compound $2NaCl \cdot CdCl_2$, and also shows the negative deviation in the neighborhood of 30~40 mole % cadmium chloride from additivity of electrical conductance[8], i. e., this system may be considered to exhibit the formation of complex ion $[CdCl_4]^{2-}$.

According to our experimental data shown in Figs. 1 and 2*, the isotherms of absorption edges of the former system show the small deviation from additivity toward longer wave length, but those of the latter system show a large deviation, especially at the neighborhood of 30~40 mole % cadmium chloride.

This fact shows that in the case of the latter system there is some evidence of complex-ion formation $[CdCl_4]^{2-}$, but not in the former system. In the case of the $NaCl$–$CdCl_2$ system, the deviation of isotherms of absorption edges toward longer wave length is not so distinct as that of the KBr–$CdBr_2$ system[5] even in the neighborhood of 30~40 mole % cadmium chloride. This fact may be explained as that the deviation of absorption edges due to the presence of complex ion $[CdCl_4]^{2-}$ is masked by the deviation of absorption edges caused by cadmium chloride which is itself a kind of associated complex[5].

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* Fig. 2 gives no data below 20% cadmium chloride because of the experimental difficulty, i. e., the melting point of samples below 20% cadmium chloride is so high that the cell is occasionally broken and the position of absorption edges of sodium chloride is shifted toward shorter wave length than that of the other component salts of the $NaCl$-$CdCl_2$ system by the previous data (H. Fesefeldt, *Z. Phys.* **64**, 741 (1930).).

Redetermination of the Crystal Structure of Calcium Cyanamide

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The crystal structure of calcium cyanamide has been studied by Dehlinger and Hanawalt, and later by Bredig[1]. Bredig reached the conclusion from his Debye-Scherrer X-ray analysis that the crystal structure of calcium cyanamide is based upon a rhombohedral lattice with $a_{rh}=5.40$ Å and $\alpha=39°55'$, which correspond to the following values for a hexagonal lattice; $a=3.67$ Å, $c=14.85$ Å. This crystal structure is similar to that of sodium azide.

The specimen used by Bredig, however, was obtained by treating calcium carbide with nitrogen. By this preparation the purity of the product can usually be reached about 70 % at the highest, always containing an appreciable amount of such impurities as calcium oxide (or hydroxide) and carbon. Accordingly, the question naturally arises as to whether pure calcium cyanamide would have the same crystal structure. For this reason the X-ray diffraction patterns of calcium cyanamide of high purity were examined.

The specimen used in this experiment was prepared from dicyandiamide and calcium carbonate according to the method enunciated by Inoue and Kanaji[2]. Dicyandiamide used was obtained by a repeated recrystallization of a commercial sample, and calcium carbonate was obtained from ammonium carbonate and calcium acetate in the presence of ammonia. A mixture of 1.5 g. of calcium carbonate and 30 g. of dicyandiamide was heated up to 770°C for 15 min. The product, white powder, was analyzed by Volhard's method[3], which revealed the product to be calcium cyanamide of 98.5% purity. X-ray diffraction patterns of this specimen were taken using an X-ray diffractometer. The experimental conditions were as follows; filtered copper radiation (Cu K_α, 1.5418 Å); 40 kV; 20 mA; scanning speed, 1/2° 2θ per min.; time con-

1) Bredig, *J. Am. Chem. Soc.*, **64**, 1730 (1942).
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stant, 4 sec.; receiving slit, 0.4 mm.; angular aperture, 1°. The mean values of the results are summarized in the Table.

TABLE

No.	2θ	d_{obs}	d_{calc}	hkl	I_{obs}	I_{calc}
1	18.05	4.91	4.90	003	0.37	0.32
2	30.43	2.94	2.94	102	1.00	1.00
3	36.55	2.458	2.45	006	0.03	0.03
4	37.20	2.417	2.417	014	0.16	0.20
5	41.62	2.168	2.166	105	0.23	0.30
6	49.28	1.849	1.849	110	0.28	0.31
7	51.92	1.762	1.757	017	0.08	0.14
8	52.91	1.730	1.731	113	0.09	0.06
9	57.77	1.596	1.593	201	0.03	0.01
10	59.06	1.564	1.565	022	0.08	0.13
11	63.19	1.471	1.469	204	0.03	0.04

Using the chart of Hull and Davey, it was possible to assign indices (hKl) to all of the observed spectra referring to a hexagonal lattice $a=3.70$ Å and $c=14.70$ Å. The calculated values for spacings from these parameters are also listed in the Table as $d_{calc.}$.

The density of the specimen was determined by a pycnometer using benzene, which gave a value 2.36 g. per cc at 25°. From the density and the lattice constants the number of chemical units contained in the unit cell was calculated as three, the calculated density being 2.19 g. per cc.

As the indices given in Column 5 are only those of such kind as $h-k+1=3n$, the translational lattice should be rhombohedral, so that the unit cell can be given as $a_{rh}=5.35$ Å and $\alpha=40°28'$. The probable space group is one of C_{3i}^{2}—R3, D_{3}^{7}—R32 and D_{3d}^{5}—R3m. These space groups give the following positions for the calcium, carbon and nitrogen atoms, referring to the rhombohedral lattice,

1Ca: 000,
1C: 1/2 1/2 1/2,
2N: xxx, $\bar{x}\bar{x}\bar{x}$.

Thus we have confirmed that the structure reported by Bredig is essentially correct. The positional parameter x for the nitrogen atoms was further refined by the trial-and-error method, the final value being 0.415. The calculated relative intensities are given in Column 7, which show a satisfactory agreement with the observed ones. It follows that the interatomic distances are C—N=1.25 Å and Ca·····N=2.45 Å.

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